KINETICS OF THE ACTIVATED SLUDGE PROCESS

by

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8. Considerations in the Process Design of Nutrient Removal Activated Sludge Processes.
G A Ekama, I P Siebritz and G v R Marais.
Water Science and Technology, 15, 3/4, 283-318, 1983.

Book

Theory, Design and Operation of Nutrient Removal Activated Sludge Processes. Tech. Trans. Document, Water Research Commission of South Africa (In Press).

CURRICULUM VITAE

PERSONAL

Name : Gerrit van Rooyen MARAIS

Nationality : South African, born 20th December 1927.

ACADEMIC QUALIFICATIONS

1955 : BSc (Eng) University of Cape Town (Civil Engineering

1963 : D I C Imperial College, London (Public Health Engineering)

1965 : MSc (Eng) University of the Witwatersrand (Soil Mechanics)

EXPERIENCE

1945-1950 : Apprenticeship as Turner and Machinist, South African Railways and Harbours, Uitenhage

1951-1952 : Lecturer in Mechanical Engineering, Port Elizabeth Technical College

1958-1959 : Research Engineer in Soil Mechanics for Anglo-American Corporation

1959-1965 : Research Engineer in Sanitation for Low-Cost Housing for the Northern Rhodesian (later Zambian) Housing Board, Lusaka, Zambia

1966 : Engineer, Department of Environmental Sciences and Engineering, University of North Carolina, Chapel Hill, in International Program for Sanitary Engineering Design (IPSED)

1967 to present : Professor of Water Resources and Public Health Enginering, University of Cape Town.

MEMBERSHIP OF SOCIETIES

South African Institution of Civil Engineers

South African Institution of Municipal Engineers

Institute of Water Pollution Control

PROFESSIONAL ACHIEVEMENTS

1970 to present : World Health Organization: appointed as Member of the Expert Committee on Environmental Sanitation

1972 : Invited as Distinguished Foreign Professor for 1972 by the American Society of Sanitary Engineering Professors

1977 : Elected Fellow of the University of Cape Town for distinguished research

1976 and 1980 : Short term Consultant to the world Health Organization in Brazil and Colombia respectively on the activated sludge process for waste water treatment

1983 : Member of Task Group on "Mathematical Modelling for Design and Operation of Biological Waste Water Treatment Works", IAWPRC

PAPERS AND OTHER CONTRIBUTIONS

THEORETICAL SOIL MECHANICS

Marais G v R (1968). Stresses in wedges of cohesionless materials formed by free discharge at the apex. Journal of Engineering for Industry, Trans ASME, Paper No 68-MH-13

LOW COST SANITATION

Marais G v R and Shaw V A (1961). A rational theory for the design of sewage stabilization ponds in Central and South Africa. Trans S.Afr.Instn.Civ.Engrs, 3, 205

Marais G v R (1961). A rational theory for the design of sewage satabilization ponds in tropical and subtropical areas. CCTA/WHO Symp.on Hyg.and Sanit.in Rel.to Housing, Niamey, Niger. (Published by Commission for Technical Cooperation in Africa, London)

Vincent L J, Algie W E and Marais G v R (1961). A system of sanitation for low-cost high-density housing. CCTA/WHO Symp.on Hygiene and Sanit.in Relation to Housing, Niamey, Niger. (Published by Commission for Technical Cooperation in Africa, London)

Marais G v R (1963). A design chart for a series of oxidation ponds treating raw sewage and some remarks on the depth of the fish pond. Trans.S.Afr.Instn.Civ.Engrs, 5, 241

Marais G v R (1963). Statistical distribution of faecal bacteria in the effluents from stabilization ponds and

some considerations in the framing of a standard for bacterial quality of the effluent. Proc.Central African Scientific and Medical Contress, Lusaka, Northern Rhodesia (Zambia)

Marais G v R (1966). New factors in the design, operation and performance of waste stabilization ponds. Bull.World Health Org, 34, 737

Marais G v R and Beer A J (1967). Measurement of dissolved oxygen concentration of oxidation ponds. Trans.S.Afr.Instn.Civ.Engrs, 9, 287

Marais G v R (1970). Overloading of Oxidation ponds. Trans.Instn.Mun.Engrs., Southern Africa

Marais G v R (1970). Oxidation ponds. Convention on Water for the Future, Pretoria.

Marais G v R (1970). A dynamic theory for the design of oxidation ponds. Proc.2nd Int.Symp.for Waste Treatment Lagoons, Kansas City, Mass.

Marais G v R and Capri M G (1970). A simplified kinetic theory for aerated lagoons. Proc.2nd Int.Symp.for Waste Treatment Lagoons, Kansas City, Mass.

Marais G v R (1971). Design of small grit channels. Trans.S.Afr.Instn.Civ.Engrs,13, 265

Marais G v R (1971). Contributed to monograph entitled Waste Stabilization Ponds by E A Gloyna. Published by WHO, Geneva

Marais G v R, Nitzche W N and Nissen L (1972). Design chart for sewers in metric units. Trans.S.Afr.Instn.Civ.Engrs, 14, 203

Marais G v R (1972). Sanitation and low cost housing. Prog.Wat.Tech, 3, 115

Marais G v R (1973). Design criteria for community waste water collection systems for developing countries. Working paper, Expert Committee on Wastes Disposal (Disp.of Community Waste Water, Geneva 25 Sept to 1 Oct, Doc.CWSS/SP/73.6

Marais G v R (1974). Faecal bacterial kinetics in stabilization ponds. Journ.Eng.Eng.Div.Proc.,ASCE, 100, 119

Marais G v R (1974). Rapporteur, "Disposal of Community

Wastewater". Rept of WHO Expert Committee, WHO Tech.Rpt.Series, No 541, Geneva.

Marais G v R (1975). Sanitation for rural and small communities. Regional Conf.on Pract.Aspects of Wat.Supply and Poll.Contr. in Southern Africa, Mbabane, Swaziland (Pub. by Nat.Inst.for Wat.Research, CSIR, Pretoria)

ANAEROBIC DIGESTION

Capri M G and Marais G v R (1975). pH adjustment in anaerobic digestion. Water Research, 9, 307

FLOCCULATION

Bratby J, Millar W and Marais G v R (1977). Design of flocculation systems from batch test data. Water S A, 3, 173

WATER CONDITIONING

Wiechers H N S, Sturrock P L K and Marais G v R (1975). Calcium carbonate crystalization kinetics. Water Research, 9, 835.

Sturrock P L K, Benjamin L, Loewenthal R E and Marais G v R (1976). Calcium carbonate precipitation kinetics, Part I - Pure system kinetcs. Water S A, 2, 101

Benjamin L, Loewenthal R E and Marais G v R (1977). Calcium carbonate precipitation kinetics, Part 2 - Effects of Magnesium. Water S A, 3, 155

Loewenthal R E and Marais G v R (1976). Stabilization of Table Mountain sandstone waters. 5th Quinquennial Regional Convention, S.Afr.Inst.Civ.Engrs. Stellenbosch (entitled: Innovation in Civil Engineering)

Wiechers H N S, Loewenthal R E and Marais G v R (1980). Lime treatment of waste water:Development and application of a single graphical technique for the chemical composition of lime treated secondary effluent. Prog.Wat.Tech, 12, Tor 347

STATISTICS

Marais G v R (1973). Statistical aids to bacteriological appraisal of effluents, Part 1 - Direct count method. Trans.S.Afr.Instn.Civ.Engrs, 16, 227

AERATION

Marais G v R (1975). Aeration devices:Basic theory, Wat.Poll.Cont. 74, 172

FLOTATION

Bratby J and Marais G v R (1973). Dissolved air flotation. Proc.Filtration Society. Conf.on "What's New in Liquid-Solid Separation", London

Bratby J and Marais G v R (1974). Dissolved air flotation. Filtration and Separation, 11, 614

Bratby J and Marais G v R (1975). Saturator performance in dissolved-air (pressure) flotation. Water Research, 9, 929

Bratby J and Marais G v R (1974). Dissolved-air (pressure) flotation-An evaluation of interrelationships between process variables and their optimization for design. Water S A, 1, 57

Bratby J and Marais G v R (1976). A guide to the design of dissolved air (pressure) flotation in activated sludge systems. Water S A, 2, 86

Bratby J and Marais G v R (1977). Flotation - Chapter 5 in book entitled Solid-Liquid Separation Equipment Scale-up, Ed D Purchas, Uplands Press, England

Bratby J and Marais G v R (1977). Dissolved-air flotation in activated sludge. Prog.Wat.Tech. 9, 311

Bratby J and Marais G v R (1977). Thickening of brown water sludges by dissolved-air flotation. Water S A, 3, 202

PROCESS CONTROL

Dold P L, Buhr H O and Marais G v R (1981). A computer-based strategy for the control of equalization tanks. Wat.Sci.Tech, 13, 349

ACTIVATED SLUDGE KINETICS

(A) Aerobic Processes

Marais G v R and Ekama G (1977). The activated sludge process, Part 1 - steady state behaviour. Water S A, 2, 163

Ekama G and Marais G v R (1977). The activated sludge process, Part 2 - dynamic behaviour. Water S A, 3, 17

Ekama G and Marais G v R (1978). Adsorption in the activated sludge process. Water S A, 4, 39

Ekama G and Marais G v R (1979). Dynamic behaviour of the activated sludge process. J.Wat.Poll.Cont.Fed, 51, 534

Dold P L, Ekama G A and Marais G v R (1980). A general model for the activated sludge process. Prog.Wat.Tech, 12, Tor 47

Alexander W V, Ekama G A and Marais G v R (1980). The activated sludge process Part 2 - application of the general kinetic model to the contact stabilization process. Water Research, 14, 1737

(b) Single sludge nitrification-denitrification process

Ekama G A, van Haandel A C and Marais G v R (1979). The present status of research in nitrogen removal:a model for the modified activated sludge process. Proc.Symp.on Nutrient Removal from Municipal Effluents. Pub.by the Water Research Comm.of S.Africa (RW 756)

van Haandel A C, Ekama G A and Marais G v R (1981). The activated sludge process Part 3 - single sludge denitrification. Water Research, 15, 1135

van Haandel A C, Dold P L and Marais G v R (1982). Optimization of nitrogen removal in the single sludge activated sludge process. Wat.Sci.Tech.,14, 443

(c) Biological excess phosphorus removal process

Siebritz I P, Ekama G A and Marais G v R (1980). Excess biological phosphorus removal in the activated sludge process in warm temperate climates. Proc.Waste Treatment and Utilization Vol 2, 233, Pergamon Press, Toronto

Marais G v R, Loewenthal R E and Siebritz I P (1983). Review: Observations supporting phosphate removal by biological excess uptake. Presented at IAWPR post-conf.seminar on phosphate removal, Pretoria, 1982, Wat.Sci.Tech., 15, 15.

Siebritz I P,Ekama G A and Marais G v R (1983). A parametric model for biological excess phosphorus removal. Presented at IAWPR post-Conf.seminar on phosphate removal, Pretoria, 1982, Wat.Sci.Tech.15,127

Ekama G A, Siebritz I P and Marais G v R (1983). Considerations in the process design of nutrient removal activated sludge processes.Presented at the IAWPR post-conf.seminar on phosphate removal, Pretoria, 1982, Wat.Sci/Tech.,15,283

BOOKS PUBLISHED

Loewenthal R E and Marais G v R (1976). Carbonate chemistry of aquatic systems, Vol 1, Theory and application. Ann Arbor Science, Ann Arbor, Michigan

Loewenthal R E and Marais G v R (1983). Carbonate Chemistry of Aquatic Systems, Vol 2, High Salinity Waters. Butterworths/Ann Arbor Science, Woburn, Mass.

Water Research Commission of South Africa (1983). Contributions to "Theory, Design and Operation of Nutrient Removal Activated Sludge Processes" (In Press)

RESEARCH REPORTS RELEASED

W 1 (1973) Capri M G "Anaerobic Filter Treatment of Wine Distillery Wastes"

W 2 (1973) Bratby J and Marais G v R "Dissolved-air (Pressure) Flotation"

W 3 Superseded by Nos 12 and 13

W 4 (1972) Loewenthal R E and Marais G v R "The Carbonic System in Water Treatment"

W 5 (1973) Wiechers H N S and Marais G v R "Calcium Carbonate Precipitation Kinetics"

W 6 (1973) Kersandt U and Marais G v R "A Mathematical Model for the Hydro-salinity Flow Systems of the Upper Berg River Basin"

W 7 (1974) Stern L and Marais G v R "Raw Sewage as Electron Donor in Biological Denitrification"

W 8 (1975) Bratby J and Marais G v R "Dissolved-air (Pressure) Flotation - an Evaluation of Interrelationships between Process Variables and their Optimization for Design.

W 9 (1975) Sturrock P L K, Loewenthal R E and Marais G v R "supersaturation and Calcium Carbonate Precipitation Kinetics"

W 10 (1975) Benjamin L, Sturrock P L K, Loewenthal R E and Marais G v R "Calcium Carbonate Precipitation Kinetics"

W 11 (1975) Wilson D E and Marais G v R "Adsorption Phase in Biological Denitrification"

W 12 (1975) Marais G v R and Ekama G A "The Activated Sludge Process Part 1 - Steady State"

W 13 (1975) Ekama G A and Marais G v R "The Activated Sludge Process Part 2 - Dynamic Behaviour"

W 14 (1975) Martin K A C and Marais G v R "Kinetics of Enhanced Phosphorus Removal in the Activated Sludge Process"

W 15 (1975) Bratby J and Marais G v R "Design Manual for Dissolved-air (Pressure) Flotation in Activated Sludge"

W 16 (1976) Bratby J and Marais G v R "Thickening of Brown Water Sludge by Dissolved-air (Pressure) Flotation"

W 17 (1976) Bratby J and Marais G v R "Dissolved-air Flotation in Water and Wastewater Treatment

W 18 (1976) Ekama G A and Marais G v R "Dynamic Modelling of the Activbated Sludge Process Series Tank Investigation"

W 19 (1977) Marsden M G and Marais G v R "Role of the Primary Anoxic Reactor in Denitrification and Biological Phosphorus Removal"

W 20 (1976) Benjamin L, Loewenthal R E and Marais G v R "The Effect of Magnesium Ions on Calcium Carbonate Precipitation"

W 21 (1977) Bratby J, Miller M W and Marais G v R "Design of Flocculation Systems from Batch Test Data"

W 22 (1977) Hoffmann R J and Marais G v R "Phosphorus Removal in the Modified Activated Sludge Process"

W 23 (1977) Vogelzang W and Marais G v R "Phosphorus Removal in the Activated Sludge Process at 14°C"

W 24 unused

W 25 (1977) Ekama G A and Marais G v R "Adsorption in the Activated Sludge Process"

W 26 (1978) Ekama G A and Maais G v R "An Experimental and Theoretical Study of the Dynamic Behaviour of the Activated Sludge Process"

W 27 (1978) Ekama G A and Marais G v R "The Dynamic Behaviour of the Activated Sludge Process" (3 volumes)

W 28 (1979) Alexander W V, Ekama G A and Marais G v R "The Contact Stabilization Activated Sludge Process"

W 29 (1979) Ekama G A, vanm Haandel A C and Marais G v R "The Present Status of Research on Nitrogen Removal:A Model for the Modified Activated Sludge Process"

W 30 (1979) Liesching P J L and Loewenthal R E "pH, Liquid Junction Potentials and Ion Pairing Constants for the Carbonate System"

W 31 (1980) van Haandel A C, Ekama G A and Marais G v R "Biological Denitrification in the Activated Sludge Process"

W 32 (1980) Rabinowitz B and Marais G v R "Chamical and Biological Phosphorus Removal in the Activated Sludge Process"

W 33 (1980) Dold P L, Buhr H O and Marais G v R "Flow and Equalization for Wastewater Treatment Plants Part 1-Development of an Equalization Algorithm"

W 34 (1980) Siebritz I P, Ekama G A and Marais G v R "Biological Excess Phosphorus Removal in the Activated Sludge Process in Warm Temperate Climates"

W 35 (1980) van Haandel C A, Ekama G A and Marais G v R "The Activated Sludge Process Part 3-Application to Single Sludge Denitrification"

W 36 (1981) B Cavalcanti van Haandel, Loewenthal R E and Marais G v R "Residual Liquid Junction Potentials in Binary Chloride Systems"

W 37 (1981) van Haandel A C, Dold P L and Marais G v R "Optimization of Nitrogen Removal in the Single Sludge Activated Sludge Process"

W 38 (1981) Arkley M J and Marais G v R "The Effect of the Anoxic Zone on Sludge Production and Settleability in the Activated Sludge Process"

W 39 (1981) van Haandel A C and Marais G v R "Nitrification and Denitrification Kinetics in the Activated Sludge Process", Vol 1 - Chapters 1-3; Vol 2 - Chapters 5 and 6

W 40 (1981) Sehayek L and Marais G v R "Supplementary Phosphorus Removed by Side-line Addition of Lime in the Activated Sludge Process"

W 41 (1981) Sehayek E and Marais G v R "Kinetics of Biological Nitrogen Removal in a Single Sludge Activated Sludge Process"

W 42 (1982) Dold P L, Buhr H O and Marais G v R "Design and Control of Equalization Tanks" Vol 1 - Chapters 1-6; Vol 2 - Chapters 7-9 and Appendices

W 45 (1982) Schroeter W D, Dold P L and Marais G v R "The COD/VSS Ratio of the Volatile Solids in the Activated Sludge Process"

W 46 (1982) Loewenthal R E and Marais G v R "Carbonate Chemistry of High Salinity Waters"

W 47 (1983) Siebritz I P, Ekama G A and Marais G v R "Biological Excess Phosphorus Removal in the Activated Sludge Process Vol 1 - Chapters 1-5; Vol 2 - Chapters 6-10; Vol 3 - Appendices

W 48 (1983) Warner A P C, Ekama G A and Marais G v R "Anoxic-Aerobic Digestion of Waste Activated Sludge"

PREAMBLE TO SUBMISSION

The research activities of the writer can be divided into three periods, research into

(1) Soils engineering, 1958-1960
(2) Low Cost Sanitation, 1960-1967
(3) Activated Sludge and Water Chemistry, 1967 to present.

The publications relevant to the work done during these periods are listed in the Curriculum Vitae where for convenience the papers are grouped under headings reflecting the subject matter.

1) Soils Engineering:

During this period the writer was employed as research engineer to the Anglo-American Corporation, at the Premier Diamond Mine, Cullinan, South Africa, under supervision of Professor J E B Jennings of the Civil Engineering Department of the University of the Witwatersrand to investigate the causes of failure of a massive wedge shaped dump, 100m high, formed by free discharge at the apex, of waste crushed diamondiferous rock.

One paper came from this investigation, describing a theoretical model of the failure.

2) Low Cost Sanitation

During this period the writer was employed as a Research Engineer to the then African Housing Board of the Government of Northern Rhodesia, Lusaka, to investigate problems with housing foundations, construction materials and sanitation. Research was oriented towards developing a low cost sanitation system that would be appropriate to the standard of public health awareness and technological competence of the communities it was to serve, and within their financial means. The research naturally divided into two tasks:

(i) Development of a water carriage sanitary system that did not require

flushing or lavatory paper, could accommodate stones, sticks and grass as cleaning material and dispose of all the waste water. This led to the development of the self topping aqua privy system discharging to (usually) small bore sewers which could be laid at extremly flat grades.

(ii) Treatment of the discharge from the aqua privy system, in oxidation ponds. The research into the oxidation pond system comprised establishment of a theoretical model to give a semi-empirical kinetic description of the biological response of the pond to the influent in terms of the retention time, temperature, wind velocity, depth and some other minor parameters. Also the kinetics of faecal bacterial die-off needed investigation to develop the most efficient pond configuration for producing an adequately low faecal bacterial effluent.

Nineteen papers dealing with the sanitation system, oxidation ponds and various other aspects ancillary to these, were published.

3) Activated Sludge and Water Chemistry Research

This research period commenced with the appointment of the writer to the Chair of Water Resources and Public Health Engineering in the Department of Civil Engineering at the University of Cape Town, 1967. Research interest developed in two main directions:

(i) Carbonate chemistry of water, and

(ii) Kinetics of the activated sludge process and aspects ancillary to the process.

(i) Research into carbonate chemistry was motivated by; corrosion problems experienced in water reticulation systems in the southern part of South Africa (where the natural waters have low pH and low TDS); corrosion problems in the Johannesburg area (where the natural waters are high in TDS, particularly in sulphate; and corrosion and precipitation problems in the reclamation of treated waste water to drinking water standard.

Resolution of problems created by these waters required research into equilibrium chemistry of the calcium-magnesium-carbonate system in low and high salinity waters and, the kinetics of precipitation and dissolution of calcium and magnesium minerals. This research produced seven papers on kinetics of precipitation and two books on calcium-magnesium-carbonate equilibrium chemistry in low and high salinity waters respectively.

(ii) Research into the activated sludge process commenced in 1969. It was motivated by the interest that developed in this process in South Africa in the latter part of the 1960's, due to the higher demands set on effluent quality. Under the writer's leadership a comprehensive investigation was inaugurated with the objective of evolving a model of this process sufficiently flexible to incorporate all the existing aerobic activated sludge process types. In 1973, with the rise in importance of biological removal of nitrate, this aspect was studied via the single-sludge nitrification-denitrification process, and included in the model. Still later, in 1975, after Dr Barnard published his findings on biological excess phosphorus removal, this phenomena also was studied, again for possible inclusion in the comprehensive model. Whereas carbonaceous degradation, nitrification and denitrification have been satisfactorily included in a general model, the inclusion of biological excess P removal to date is only partial and still requires ancillary, semi-empirical treatment to describe the behaviour.

Developments in the model were reported in 13 papers, and in a contribution to a design manual written on the request of the Water Research Commission.

Additional to the kinetic work on the activated sludge process, research was undertaken into thickening of the waste sludge by flotation. This research was reported in 7 papers plus a chapter on flotation in a book on liquid solid separation.

Some miscellaneous papers dealing with statistics, aeration and anaerobic digestion were also published.

MATERIAL SUBMITTED

The writer decided to submit, for the purposes of the degree, a selection of the more important papers on the kinetics of the activated sludge process. These papers chronologically trace developments in the kinetic theory, from aerobic steady state behaviour to aerobic, nitrification and denitrification behaviour under cyclic flow and load conditions in multi-reactor systems including aerobic, anoxic and anaerobic reactors. Also included are papers reporting research, on biological excess phosphorus removal. Application of the research to design is illustrated by including a copy of a design manual written for the Water Research Commission of South Africa, to which the writer and his group made a major contribution.

The reader will note that not a single contribution in the list selected was written by the writer alone, however, the research undertaken at the University of Cape Town in the fields described above was carried out under his direction. In this endeavour approximately 35 students participated, over a period of 14 years, to the common purpose of fulfilling the overall objectives set initially. The multiplicity of aspects to which attention had to be given is evident from the research reports listed in the Curriculum Vitae.

In reading through the papers submitted one will notice that, due to the long time span over which they were written, ideas necessarily changed, and it may not be easy at times to see the common thread that passes through all. For this reason it was thought useful to give a review of the considerations that entered into setting up a model describing the kinetics of carbonaceous material degradation. This model forms the foundation on which denitrification and biological excess phosphorus removal are readily grafted; understanding of the carbonaceous degradation model facilitates understanding of the other two phenomena.

KINETICS OF CARBONACEOUS MATERIAL REMOVAL IN THE ACTIVATED SLUDGE PROCESS

INTRODUCTION

The time-variant nature of the inputs to a wastewater treatment plant requires that the dynamic response of the microbial culture be considered in order to predict process performance realistically. An ability to model process behaviour in the field of wastewater treatment is important for three reasons: (1) to overcome problems encountered in the operation and control of treatment facilities; (2) to aid in the development of optimal design procedures; and (3) to provide a means for developing in-plant control strategies.

Wastes from municipal sources principally of domestic origin invariably conform to daily cyclic patterns of flow and concentration. The waste consists largely of naturally-occurring organic materials which are well-balanced for microbial growth. In contrast, wastes from industrial sources are unpredictable with regard to flow and concentration patterns; the waste may contain constituents that differ significantly in chemical structure from those occurring naturally, which the organism mass cannot metabolize, or only partially metabolize, over the period of residence in the plant; highly specific organism masses may need to be developed to treat the waste; deficiencies in nutrients for balanced growth are common and the waste may contain inhibitory and poisonous organic substances. Furthermore, the unpredictable nature of the load discharge may subject the organism mass to violent changes in loading rate and chemical constitution.

Whereas it is possible to generalise on the treatment of municipal waste flows of principally domestic origin, this is not so for industrial waste flows. Each industrial waste, to a greater or lesser degree, has components unique to itself that require specific action for

resolution based on experimental enquiry or experience.

Municipal waste flows will virtually always contain an industrial component but provided the component is limited the response of the process should not deviate significantly from that of a purely domestic waste flow for reasons of dilution by, and the usually adequate supply of essential nutrient factors from the dominating domestic waste component.

Municipal waste of principally domestic origin contains a complex mixture of organic materials, some of which are readily biodegradable, some slowly biodegradable and some quite unbiodegradable in terms of the residence time in the process; the organic material also is in soluble, colloidal and particulate form. The organism mass constitutes a complex mixture of microorganisms which responds sensitively to the process inputs and environmental conditions.

Modelling of the activated sludge process has been influenced significantly by the kinetic growth studies of pure cultures grown on soluble substrates; there is no denying the positive influence these have had, but criticism can be levelled at the too often uncritical way in which the findings of the pure culture kineticists have been applied to describe the kinetics of the activated sludge process. It is necessary therefore to review the concepts that have developed from pure culture studies and see in what fashion these need to be modified in order to be applied to mixed cultures with multicomponent organic substrate sources as encountered in the activated sludge process.

In this paper the considerations that have entered or need to enter into modelling the activated sludge process treating waste flows of predominantly domestic origin will be discussed. Only carbonaceous material degradation will be dealt with as modelling of the kinetics of this material is the central problem in the activated sludge process. Once a model for this material is established or accepted, modelling of nitrification, denitrification, biological excess phosphorus removal and other ancillary phenomena can be grafted into the carbonaceous model in such a manner that inconsistencies do not arise. It is of crucial importance therefore that the carbonaceous model is consistent in itself and provides such flexibility that these other effects can be incorporated readily.

PURE CULTURE INVESTIGATIONS

The first major contribution to the kinetics of microbial growth on soluble substrates appears to have been developed by Penfold and Norris (1912). They proposed an equation linking the doubling time of bacteria to the concentration of substrate surrounding the organism which, if appropriately transformed, is identical to that proposed later by Monod (1942). The work of Penfold and Norris, however, seems to have been premature to the needs of the time and little or nothing was done to develop their hypothesis further.

To Monod must be credited the inauguration of a period of intensive development of the kinetics of microbial growth, a process that has continued to this day. Monod specifically limited his enquiry to the "...positive phases of growth, since the study of bacterial 'death' i.e. of the negative phases of growth, involves distinct problems and methods". He proposed two important relationships with respect to organism growth:

(1) The mass of organisms generated is proportional to the mass of substrate utilized i.e. the specific "yield" is constant for a particular substrate

$$M\Delta X = Y.M\Delta S \qquad (1)$$

where Y = specific yield constant (mass bacteria formed per unit mass substrate utilized)

$M\Delta X$ = mass of organisms generated

$M\Delta S$ = mass of substrate utilized

(2) The specific growth rate, μ, is linked to the concentration of the limiting substrate, S, surrounding the organism by the expression

$$\mu = \mu_m S/(K_s + S) \qquad (2)$$

where μ_m = maximum specific growth rate constant

K_s = saturation constant numerically equal to the substrate concentration at which the growth rate is one-half the maximum value.

With regard to Eq (2), Monod accepted it as an empirical relationship "...to express conveniently the relation between exponential growth and concentration of an essential nutrient". He admitted that several mathematically different formulations could serve equally well, but adopted Eq (2) because it was "...similar to an adsorption isotherm or the Michaelis equation". He ascribed the magnitude of μ_m to the activity of specific enzyme systems involved in the breakdown of different compounds and that K_s "...bear some more or less distant relation to the apparent dissociation constant of the enzyme involved in the first step of breakdown of a given compound. Furthermore, since a change of conditions affecting primarily the velocity of only one rate determining step will, in general (but not necessarily) be only partially reflected in the overall rate one may expect C_i [our K_s] values to be lower than the corresponding values of the Michaelis constant of the enzyme catalyzing the reaction". He recognised complex growth cycles with sequential growth rates, μ, separated by angular transition points on a log (growth rate)-time plot. This he interpreted as addition or removal of one or more rate limiting steps resulting from a change in the composition of the medium or from transitory accumulation of a metabolite which essentially serves as a secondary nutritional source. Where the organic source is the limiting factor and is constituted of a mixture of one or more organic compounds, if one of the constituents acts inhibitory on the enzyme attacking the other, the one constituent will be used exclusively until exhausted whereupon the enzyme system for the next becomes operative - sequential growth phases are exhibited, separated by a period in which the growth rate decreases to a minimum.

From the findings of Monod it is evident that the biodegradation reaction and its rate, as manifested by the growth rate observed, is the consequence of a complex web of enzymatically catalyzed reactions that may

be modelled empirically by Eq (2), but not necessarily so; deviant behaviour may be observed due to inhibition of enzymes, secondary product formation and other factors.

Consideration of Eqs (1 and 2) will indicate that growth behaviour conforming to these relationships in fact implies the following:

Equation (1) implies:

(1) No organism mass loss occurs subsequent to synthesis;
(2) No storage of substrate (internal or external to the organism) occurs.

Equation (2) implies:

(1) The rate of substrate transfer is not influenced by substrate inhibition or the rate of substrate diffusion;
(2) No external storage of substrate takes place prior to transfer through the cell wall;
(3) The substrate is metabolized directly, i.e. no internal storage takes place;
(4) One enzyme system catalyzes the growth reaction;
(5) All the factors necessary for growth are present, and only substrate is growth limiting.

The implications under Eqs (1 and 2) have been subjected to extensive investigation to evaluate their relevance and limitations. Most of the research has involved steady state studies of continuous culture generally carried out using the chemostat. This apparatus [called the "bactogen" by Monod (1950)], comprises a completely mixed constant-volume flow-through reactor operated by controlling the flow rate of culture medium into the vessel; it was first proposed by Monod (1950) and Novick and Szilard (1950). The flow-through reactor process is particularly useful because (1) the concentrations of organisms, X, and substrate, S, in the effluent are equal to the respective concentrations in the reactor, and (2) if the influent substrate concentration, S_i, and flow rate, Q, and volume, V, are held constant then a steady state develops, and

$$\mu = D$$

where D =dilution rate (Q/V), equal to the reciprocal of the hydraulic retention time, R.

From mass balances on organisms and substrate, and using Eqs (1 and 2), it was possible to derive the following equations to define the behaviour of a continuous culture in the chemostat:

$$dX/dt = \left(\mu_m S/(K_s+S) - D\right) \tag{3}$$

$$dS/dt = D(S_i-S) - (1/Y)\left(\mu_m S/(K_s+S)\right)X \tag{4}$$

At steady state (constant S_i, Q, V) the concentrations of organisms and substrate reduce to:

$$X = Y(S_i-S) \tag{5}$$

$$S = K_s\left(D/\mu_m-D)\right) = K_s\left(1/\mu_m R-1)\right) \tag{6}$$

Equations (5 and 6) provide the basis to develop a graphical interpretation of predicted chemostat operation for selected values of S_i, μ_m, K_s and Y by plotting X and S versus dilution rate, D, as shown in Fig 1.

Yield of Aerobically Grown Organisms

Monod demonstrated that the total cell yields for several aerobically grown heterotrophs were linearly proportional to the quantity of either meat extract (as a complex nutrient) or carbohydrate (as a simple nutrient) in a basal salts medium: hence Eq (1):

$$M\Delta X = Y.M\Delta S$$

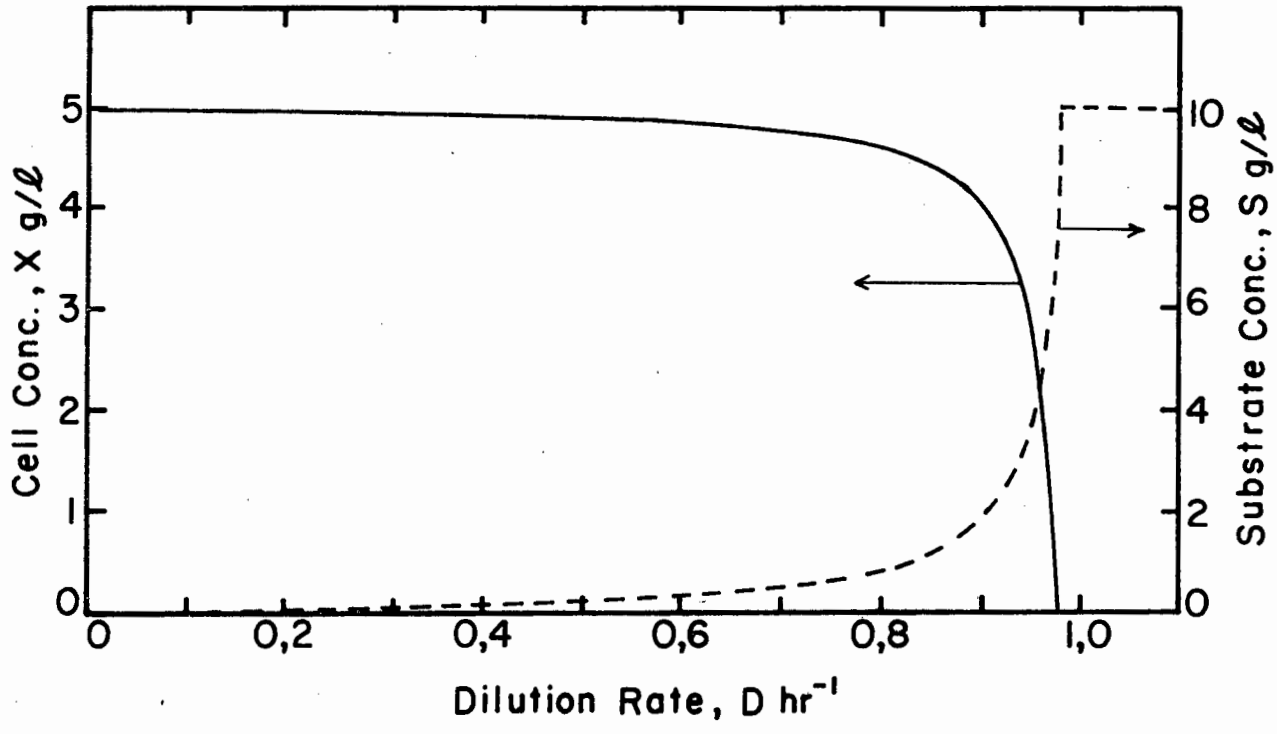

Fig 1 Steady state substrate and cell concentration as a function of chemostat dilution rate; values based on Monod's postulates with μ_m = 1,0 h^{-1}, Y = 0,5, K_s = 0,2 g/ℓ and S_i = 10 g/ℓ.

Equation (1) is of great basic importance but suffers the limitation that the specific yield constant, Y (as mass cells formed per mass substrate utilized), is unique to the particular substrate and, possibly, to the organism assembly. Subsequent to the work of Monod, with interest developing in commerical production of certain microorganisms for which the substrate may not be a constant well-defined chemical entity, research was focussed on seeking a parameter in terms of which the yield would (perhaps) be relatively constant with respect to the parameter change and independent of organism type. From the literature it would appear that four parameters have emerged: i.e. yield based on

(1) carbon content of the substrate (Y_C);
(2) electron donor capacity of the substrate ($Y_{av\ e'}$);
(3) total oxidative energy of the substrate (Y_{kcal}); and
(4) ATP production per mole of substrate (Y_{ATP}).

An incisive review of yield characteristics of heterotrophs was published by Payne (1970), which sheds considerable light on the respective utility of the parameters (2) to (4), above. Payne does not deal directly with (1), but from the considerations presented later it will be shown that this parameter potentially is not as useful as the other three. However, it is deliberately retained for discussion because in activated sludge kinetics the total organic carbon content of substrate on occasion has been suggested as a basic parameter in terms of which to describe growth kinetics:

(1) Siegel and Clifton (1950) found that in batch cultures of E.coli grown on glucose, the fraction of carbon assimilated with respect to the total carbon removed from the culture medium was relatively constant (0,56 to 0,60) irrespective of whether the growth was in the lag phase or at different times in the logarithmic growth phase. Herbert (1958) obtained data consistent with the above in studies of the growth of Aerobacter aerogenes and Aerobacter cloacae in continuous culture over a wide range

of dilution rates using glycerol as substrate. The output of cells was directly proportional to the quantity of glycerol utilized, with a fraction 0,61 of the substrate carbon assimilated in synthesis. MacKechnie and Dawes (1969) grew Psuedomonas aeruginosa on glucose, gluconate and 2-oxo-gluconate and found 0,58, 0,59 and 0,64 of the substrate carbon assimilated. The constancy of the fraction of substrate carbon incorporated in cells would direct one to the opinion that the carbon content of a substrate can be a useful measure for describing growth. Before raising objections to this conclusion it is preferable to discuss the three other approaches.

(2) Any organic substrate can be characterised by its number of electrons available for transfer. The number of electrons available per mole of substrate is determined by

a) writing the balanced chemical equation for complete combustion of one mole of substrate to determine the number of moles of oxygen consumed, and
b) multiplying the number of moles of oxygen by four (which is the number of electrons required to reduce one mole of oxygen).

For example, a mole of glucose requires 6 moles of oxygen for complete oxidation and 24 electrons are transferred i.e. glucose is a 6 mole (192g) oxygen or 24 available electron compound:

$$C_6 H_{12} O_6 + 6O_2 \rightarrow 6 CO_2 + 6 H_2, \text{ and}$$
$$6 \cdot 4 = 24 \text{ available electrons.}$$

Lists of available electrons for a wide range of organic compounds have been prepared by Kharasch (1925, 1929) so that usually it is not necessary to do an analysis as that above.

Where the substrate constitution is not known its available electrons can be determined experimentally by the Total Oxygen Demand (TOD) or Chemical Oxygen Demand (COD) test. The more widely known test is the COD; applied to glucose, for example, the mass of oxygen required

for complete combusion of one mole of glucose is 6.32 = 192g COD. Hence

1 available electron (1 av e') ≡ 192/24 = 8g COD.

Payne (1970) analyzed approximately 120 experiments involving pure cultures grown on pure substrates and 30 experimental involving mixed cultures grown on pure substrates. He accepted the data as reported "with no concern for influences that might be noted if maintenance energy were considered or if some component(s) other than energy source were made limiting". These experiments all gave near constant values for the yield of cells per substrate available electron ($Y_{av\ e'}$) with a mean $Y_{av\ e'}$ of 3,03g cells/av e' for pure cultures and 3,14g cells/av e' for mixed cultures. These values expressed in terms of COD (Y_{COD}) would be respectively 3,03/8 = 0,38 and 3,14/8 = 0,39 gram cell mass per gram COD removed from the medium.

(3) The third approach to quantifying yield is the relationship between the energy of combustion of the organism mass and that of the substrate removed. As early as 1922 Terroine and Wurmser found that the fractional conversion of the substrate energy to organism energy was 0,60. In 1967 Mayberry, Prochazka and Payne, in developing a thermodynamic model for growth of heterotrophs, determined the heat of combustion of dried cells grown aerobically as 5,3 kcal per gram dry weight (i.e. for Terroine and Wurmser Y_{kcal}= 0,60/5,3 = 0,113g cell mass per kcal substrate). Mayberry et al. (1967) estimated the heat lost in the transformation of substrate to organism mass by multiplying the moles of oxygen consumed per mole of substrate utilized by 106 kcal/mole (the value of 106 is the average quantity of energy available from the transfer of four electron equivalents from an organic source to reduce one mole of O_2; Mayberry et al. 1967, 1968). Accepting these results, Payne (1970) calculated the yield in grams cells per kilocalorie involved (where the kcal involved is given by the energy in the organism mass plus the energy lost in the reduction of the oxygen) to give a yield in grams cell mass per kcal, Y_{kcal}. Again the values of Y_{kcal} were remarkably near constant for a wide range of substrates and organism types; for growth on single

substrates 40 experiments involving pure cultures and 32 experiments involving mixed cultures gave mean values of 0,116 and 0,110g cell mass/kcal, respectively.

(4) The fourth approach to quantifying yield involves relating the yield of cells to the amount of ATP formed during growth i.e. Y_{ATP}. Bauchop and Elsden (1960) found that in anaerobic growth of S. faecalis and some other organisms the yields in grams dry weight were directly proportional to the moles of ATP produced per mole of energy source catabolized; these Y_{ATP} values averaged 10,5g cells per mole of ATP generated, with a range of 8,3 to 12,6. Calculation of the molar ATP production was based on prior knowledge of pathways employed by the organism for the catabolism of glucose, ribose and arginine. With regard to aerobic growth, Payne (1970) states that "...molar production of ATP in aerobic cultures may only be estimates and not determined". Attempts at relating ATP production to cell yield under aerobic conditions have included ATP gains based on (i) oxygen consumed, (ii) values for P/O ratios obtained with cell-free extracts, and (iii) "fragmentary knowledge of the components of the electron chain in the organism under study" (Payne, 1970). There is little merit in describing in detail the considerations that entered into Payne's analysis: he arrives at the relationship $Y_{ATP} \simeq 10,60$g cells/mole ATP from analysis of results from a number of substrate-organism growth experiments. The fact that Payne obtained values of Y_{ATP} similar to the 10,5 of Bauchop and Elsden (1960) is not surprising perhaps, as Payne's values were based on assumed ATP gains: in fact, he concedes that the individual Y_{ATP} values "...were obtained by treatment of the data with an answer in mind".

Servizi and Bogan (1963,1964), on the strength of Bauchop and Elsden's association of ATP production and cell yield, assumed that the ATP produced was proportional to the "free energy of oxidation" of the substrate, and since the free energy of a substrate is related to the moles of oxygen consumed in oxiding one mole of substrate, concluded that the yield was proportional to the substrate COD removed from the medium.

Evaluating the four approaches discussed above, the Y_{ATP} approach probably is important in unravelling the internal mechanisms of growth,

but has little value in practical modelling of growth. The Y_{kcal} approach similarly presents certain practical difficulties, but does contribute in that it demonstrates that the energy changes in growth are closely proportional to the available electron changes. The $Y_{av\ e'}$, cum Y_{COD}, approach appears to be the indicated one because it expresses the yield in terms of a measureable chemical entity, the number of available electrons, which can be readily measured via the COD test. Thus, the description of the activated sludge process in so far as it affects carbonaceous material removal is essentially a description of available electron behaviour. That this description is also closely linked with the energy behaviour is of conceptual interest, but not directly of crucial or practical importance in modelling the process.

With regard to the first approach, of accepting the constancy of the fraction of substrate carbon incorporated in cells (i.e. the Y_C approach), it should be noted that the ratio

$$\frac{\text{mass substrate carbon}}{\text{substrate available electrons}}$$

can be different for different organic compounds. Therefore, accepting the observed constancy of $Y_{av\ e'}$ for a wide range of organic compounds, and noting the variability in the above ratio, the corresponding Y_C values will not be constant: i.e.

$$Y_C(\text{g cells/g substrate C}) = Y_{av\ e'}(\text{g cells/av e'}) * (\text{av e'/g substrate C})$$

$$\downarrow \qquad\qquad \downarrow$$

constant variable

This is illustrated in Table 1, using data for Y_{sub} (g cells/mole substrate) and Y_{kcal} (g cells/kcal) for five substrates from Payne (1970), and calculating Y_{COD}, $Y_{av\ e'}$ and Y_C. An examination of Table 1 shows that whereas Y_{kcal}, $Y_{av\ e'}$ and Y_{COD} are consistent with each other throughout, the Y_C values range from 0,86 to 1,51 g cells per gram substrate carbon. Therefore, carbon should not be accepted as a basis

Table 1: Comparison of Y_{kal}, $Y_{av\ e'}$, Y_{COD} and Y_C for different substrates (Observed Y_{sub} values after Payne, 1970).

Organism	Substrate	Y_{sub} (observed)	av e'/mole	gC/av e'	$Y_{av\ e'}$	Y_{COD}	Y_{kcal}	Y_C
Psuedomonas $C_{12}B$	Phenylacetate	111,0	36	2,67	3,08	0,39	0,113	1,16
	Succinate	42,3	14	3,43	3,02	0,38	0,113	0,88
	Dodecanol	217,0	72	2,00	3,01	0,38	0,112	1,51
Psuedomonas aeruginosa	Glucose	76,2	24	3,00	3,18	0,40	0,114	1,06
	2-Oxogluconate	62,0	20	3,60	3,10	0,39	0,118	0,86

Units: Y_{sub} - gram cells per mole substrate utilized

$Y_{av\ e'}$ - gram cells per substrate available electron

Y_{COD} - gram cells per gram substrate COD

Y_{kcal} - gram cells per kcal substrate

Y_C - gram cells per gram substrate carbon

parameter to describe aerobic growth of organisms. The apparent confusion over Y_C appears to have arisen because the organic material investigated by Siegel and Clifton (1950), Herbert (1958) and MacKechnie and Dawes (1969) fortuitously all have very similar ratios of carbon to available electrons, close to 3, and therefore exhibit near constant Y_C values.

Organism Mass Loss

An important deviation from the theoretical prediction of chemostat behaviour derived from Monod's postulates, Eqns (3 and 4), is that the specific yield, Y, apparently decreases as the dilution rate, D, decreases or, equivalently, as the organism retention time increases. Herbert (1958) reported this response for a number of organisms, as illustrated in Fig 2 for Aerobacter aerogenes grown on glycerol.

Two hypotheses have been advanced to explain this behaviour: Endogenous metabolism, Herbert (1958); and Maintenance energy, Pirt (1965).

Endogenous Metabolism: Herbert, accepting Monod's concept of constant cell yield, proposed that the most probable explanation for the reduction in specific yield with increasing organism retention time is that, in addition to the anabolic metabolism of the organisms (conversion of substrate to cell mass), the organisms also have a constant specific endogenous metabolism in which cell material is oxidized to CO_2. Herbert expressed this mathematically by incorporating a first order decay term in the growth rate equation, viz.

Growth : $(dX/dt)_g = \mu X$ (7)

Endogenous metabolism : $(dX/dt)_e = -bX$ (8)

Net growth : $dX/dt = \mu X - bX = (\mu - b)X$ (9)

Note: the substrate change is derived by using Eq (1) applied only to the growth term i.e.

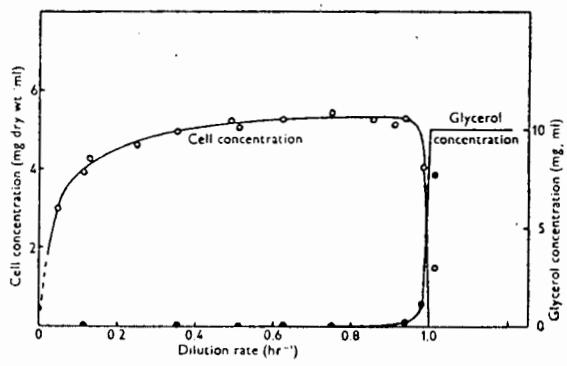

Fig 2 Growth of Aerobacter aerogenes in continuous culture with glycerol as limiting substrate (after Herbert, 1958).

$$dX_g = Y\ dS$$

Inserting in Eq (7):

$$dS/dt = (\mu/Y)X \qquad (10)$$

It should be noted that some authors have applied Eq (1) to both Eqs (7 and 8) [i.e. Eq (9)] which is incorrect.

Inclusion of the b term for endogenous metabolism in the formulations describing chemostat response [Eqns (3 and 4)] enabled Herbert to predict the variation in cell concentration apparently very accurately: at low growth rates (low D) endogenous metabolism becomes more important compared with the anabolic metabolism and the "effective" cell yield, $M\Delta X/M\Delta S$, decreases. This approach has been used widely to describe the behaviour of organisms in the so-called "negative growth rate phase". An important implication of Herbert's formulation is that the endogenous metabolism is independent of the growth metabolism.

Maintenance Energy: Duclaux (1898) appears the earliest microbiologist to propose the concept of a maintenance energy requirement; in contrast to Herbert, he postulated that the substrate energy is utilized both for growth purposes and for maintenance of essential organism functions. Pirt (1965) accepted the Duclaux hypothesis of a maintenance energy in preference to the endogenous metabolism approach of Herbert which he described as "...artificial and indirect". He defined "energy of maintenance" of bacteria as energy substrate consumed for functions other than production of new cell material. He qualified this approach by assuming that substrate would be available for maintenance energy requirements. The rate of abstraction of substrate was accepted to conform to Monod's rate equation, Eq (2), but the fate of the substrate was twofold: A fraction of the total substrate absorbed (dS) is utilized by the existing organism mass for maintenance (dS_m) and the balance (dS_g) is utilized for generation of new cell mass (dX) i.e.

$$dS = dS_g + dS_m \tag{11}$$

The yield observed therefore is given by

$$Y_{obs} = \frac{dX}{dS} = \frac{dX}{dS_g + dS_m} \tag{12}$$

Pirt assumed that the rate of demand of substrate for maintenance is proportional to the concentration of existing organisms i.e.

$$dS_m/dt = mX \tag{13}$$

Comparing Herbert and Pirt's approaches, Herbert assigns the substrate utilized totally to active mass generation and thereafter an organism mass loss occurs with time due to oxidation of the metabolic material. Pirt assigns the substrate in part directly to growth and in part directly to maintenance of essential organism functions, the fraction assigned to essential functions depending on the mass of organisms already present. Herbert's approach implies that an organism, as its age increases, reduces in mass; Pirt's approach implies that the organism is kept in a stable state by regenerating the mass lost due to maintenance, and in effect no mass loss occurs.

Both concepts were proposed on the basis of what the respective authors surmized as a logical explanation for the observed reduced yield. Each enables the observed organism mass concentrations to be more accurately predicted than by the use of Monod's hypotheses. In assessing the usefulness of the respective hypotheses one method is to apply each to conditions outside the range in which they were developed: for example, when the influent substrate supply to the chemostat and/or the oxygen supply is stopped.

(1) Substrate supply stopped. When no substrate is fed to a culture of organisms it is well known that the mass of organisms will decrease

with time. This phenomenon has been referred to by microbiologists as early as 1936 (Woodridge and Standfast). With regard to the Pirt approach, no explanation is provided for this phenomenon; there is no external source of energy for channelization to the maintenance function, and Pirt's hypothesis can no longer be applied. Under these conditions a qualitative change in organism response from that of Pirt to some other will be necessary. In contrast, Herbert's approach does allow account for the decrease in organism mass in the absence of substrate feed because the decrease in cell mass is formulated independent of the substrate input. Of course it is not unreasonable to expect that when there is no longer substrate present a qualitative change in the organism response may take place. In the absence of greater clarity as to the causes of endogenous mass loss one is forced to accept that hypothesis which explains this decrease without requiring the necessity for a qualitative change in behaviour. In this respect, Herbert's approach is clearly superior.

(2) Oxygen supply stopped. In experiments on mixed cultures, if the culture is deprived of oxygen periodically the mass loss does not appear to differ from that under continuous aerobic conditions. Under these circumstances it is not possible to apply Herbert's hypothesis logically because during the zero oxygen state no electron acceptor is available for endogenous energy generation and again a qualitative change in behaviour during the zero oxygen phase is necessary to explain the observed phenomenon.

The kinds of argument advanced in (1) and (2) above are not necessarily persuasive because the qualitative changes in environment could induce qualitative changes in response. However, there are other phenomena which are not explained by these theories. For example, it seems to be well attested that in aerobic digestion of an organism mass, the reduction in mass is associated with a concomitant accumulation of inert organic material - a phenomenon totally ignored by both theories. This phenomenon cannot be disregarded and should be part and parcel of any hypothesis on endogenous mass loss if the hypothesis is to lead to a

realistic description of the organism behaviour.

In searching for an alternative hypothesis it should be noted that, in pure cultures it is commonly accepted that under no substrate addition organisms will die; little information on the rate of death is to be found in the literature. However, irrespective of the rate of death, one could postulate that on death a part of the organism mass is unbiodegradable material, which would explain the generation of inert material. The remaining part is biodegradable and could be utilized either for maintenance or as a substrate source for growth; at present there appears to be no information as to the relative magnitude of these two effects, there is little merit, therefore, in attempting to delineate the behaviour more exactly. However, the considerations above, when applied to mixed cultures (later), does allow the establishment of a consistent approach to the phenomenon of endogenous mass loss, incorporating the behaviour of aerobic organisms under conditions of no influent substrate and no oxygen (or other exogenous electron acceptor) supply, and the phenomenon of inert residue accumulation.

In examining the various hypotheses on endogenous mass loss it is appropriate, perhaps, to remember the words of Monod (1949) that "...the negative phase of growth involves distinct problems and methods". This view is reflected on in the proceedings of the 1976 Symposium of the Society of General Microbiology on "The Survival of Vegetative Organisms", in which it was concluded that very little is known of the death or declining growth phase (Trinci and Thurston, 1976).

Growth versus Storage Under Transient Conditions

Monod's Eq (1) states that $M\Delta X = Y.M\Delta S$, and that Y is a constant. This, as stated earlier, implies that no external or internal storage of substrate occurs because if it did, then under certain conditions the specific yield constant, Y, would not remain fixed in value.

Daigger and Grady (1982), in reviewing the dynamics of microbial growth on soluble substrates, concluded that Y did not always appear to be constant; this was noted specifically under transient conditions. In analyzing this phenomenon they subdivided transient behaviour into growth

responses and storage responses, respectively. These two responses were categorized as follows:

(1) Growth response: transport of extracellular substrates into the cell, oxidation of a portion to obtain energy, and use of the other portion for synthesis of the components of the biomass in the "proper" proportions.

(2) Storage response: substrate is no longer only utilized for synthesis of protoplasm, and synthesis of polymers occurs, these being stored by the organism as carbohydrates or lipids.

The major differences between the two responses are (1) the nature of the material synthesized (protoplasmic or storage polymer), and (2) the mass of substrate oxidized per unit of biomass synthesized, this ratio being significantly greater for protoplasm formation than for storage product formations.

The distinction of Daigger and Grady between growth and storage responses identifies a crucial experimental parameter in any study of the dynamics of microbial response: namely, oxygen utilization rate (OUR). For example, for a culture under transient conditions (either in a continuous flow or batch experiment), if over a short interval

(a) the mass of substrate COD utilized can be accounted for in terms of the change in cellular COD and the amount of oxygen utilized (i.e. a COD mass balance is satisfied); and if

(b) the observed cell yield (and thus the budgetting of substrate COD between synthesis and oxidation) is in accord with Eq (1) of Monod (i.e. constant Y);

then it is possible to state that no storage has occurred.

The above observation highlights the importance of the COD mass balance (which requires measurement of OUR) in providing the fundamental experimental basis for any study of transient behaviour. However, the

literature shows that this requirement has seldom been met; consequently much of the published data on transient behaviour is of limited utility, with interpretation uncertain.

Growth Kinetic Response: Accepting that mass balances are assured, two types of growth-time response have been observed:

(1) Growth Rate Hysteresis (GRH), proposed by Perret (1960): during periods when the substrate concentration varies, the specific growth rate of the culture tends to lag behind the value predicted by the steady state specific growth rate-substrate relationship.

(2) Available Reaction Potential (ARP), proposed by McLellan and Busch (1969): during periods when the substrate concentration varies, the specific growth rate immediately follows the value predicted by the steady state μ-S relationship.

Daigger and Grady (1982) provide extensive evidence for the existence of GRH and ARP under transient conditions as separate phenomena and in combination. These authors also provide a plausible explanation for the phenomena in terms of physiological adaption of the culture to changing environment; to summarize:

> Levels of RNA, enzymes, etc. adapted to an environment at steady state are less than the values attainable at the maximum specific growth rate. When a transient is applied the culture cannot immediately grow at its maximum rate; however, the levels of RNA, enzymes, etc. change gradually with time, to reach the maximum values possible for the new growth condition - hence GRH. In addition Koch and Deppe (1971) have shown that cultures grown at low μ possess "extra" RNA which becomes immediately active when the organisms are subjected to a step increase in substrate concentration - hence ARP.

Storage Response

Storage of polysaccharide or lipids can occur when growth of a

culture is limited by a biosynthetic restriction in the presence of a readily utilizable carbon and energy source. The first observation of storage appears to be that of Holme and Palmstierna (1956). They grew Escherichia coli in a simple glucose-ammonium salt medium; when ammonia was limiting, the glycogen content increased markedly during the final stages of growth. Similar responses have been observed for both glycogen and PHB storage under nitrogen-limiting conditions, e.g., Holme (1957), Macrae and Wilkinson (1958), Doudoroff and Stanier (1959), Wright and Lockhart (1965).

The deficiency in nitrogen for metabolic purposes need not arise necessarily from an imbalance in the nitrogen-carbonaceous material ratio; storage can occur even with excess nitrogen. For example, with very high concentrations of carbonaceous material the rate of nitrogen transfer into the cell may not be sufficient to match the rate of transport of carbonaceous material. This imbalance also can lead to storage. One solution found by Ekama and Marais (1982) was to increase the nitrogen concentration substantially above that required for metabolic purposes, thereby increasing the rate of nitrogen transfer into the cell.

It is of interest to note that storage of glycogen and PHB appears to have been observed only in laboratory activated sludge acclimated to carbohydrates (usually glucose). Several attempts to demonstrate storage in full scale activated sludge plants have been unsuccessful (van Gils, 1964; Painter, Denton and Quarmby, 1968; Deinema, 1972).

The significance of the pure culture response discussed in this section needs to be assessed in modelling the activated sludge process. If phenomena such as storage were the general case then deviations from Monod's hypotheses would have been common, whereas the opposite is true. The information was developed principally under conditions of high growth rate, or equivalently at very short sludge ages (< 12 hours). The sludge ages normally expected in activated sludge processes are very unlikely to be less than one day; under such conditions storage response at odds with Monod's hypotheses is unlikely to arise.

One possible situation, however, could be conceived that could lead to storage effects: Jenkins and co-workers (Lee, Koopman, Jenkins

and Lewis, 1982) proposed a process configuration in which a small "selector" reactor receiving the influent and recycle flows precedes the main reactor; the configuration was proposed as a means for reducing the possibility of filamentous organism growth. If the soluble substrate concentration in the "selector" reactor is high then problems of nitrogen transfer limitations may lead to storage of substrate; however, this can be overcome by significantly increasing the nitrogen concentration in the influent.

Diauxic Growth

Monod (1949) appears to have been the first to report that in batch culture of a specific species of bacteria exposed to two carbon energy sources, one was utilized for growth to exhaustion, followed by a lag in growth after which the other carbon source was utilized. Since the report of Monod this growth pattern has been observed repeatedly and the phenomenon is termed diauxie. In reviewing this growth pattern, Harder and Dijkhuizen (1976) found that diauxic growth is exhibited when (1) adaption to the less preferred substrate is prevented by the preferred, and (2) the process of adaption to the less preferred takes place under "non-gratuitous" conditions. Should these conditions not be met the substrates are utilized either simultaneously or sequentially but without an intervening lag phase. This phenomenon, according to Dyson (1974) finds its origin in the regulation of enzyme synthesis and activity.

With the same substrate mixture, one organism may exhibit diauxie but another not. In chemostat studies at high dilution rates, initially an organism may exhibit diauxie, indicated by preferential utilization of one substrate. After prolonged operation, however, the organism might adapt to utilize both substrates equally effectively. At low dilution rates it seems to be a general observation that both substrates are utilized simultaneously. This led Harder and Dijkhuizen (1976) to suggest "...that concurrent utilization of such compounds in nutritionally poor natural environments is a general phenomenon".

Studies on mixed cultures receiving a mixed substrate are difficult because the population structure changes due to selection - a

behavioural pattern also true for single substrates. Generally the response of mixed culture/mixed substrates is more variable but the basic behaviour pattern with regard to diauxic growth is not at variance with single organism/mixed substrate reponse. At low dilution rates again the concurrent utilization of substrates is general but the rates of utilization may differ so that the substrate that induces the higher growth rate would appear to be utilized preferentially.

In the activated sludge process the dilution rate usually is so low, even in highly loaded plants, that diauxic growth is unlikely; that is, simultaneous utilization of all substrates can be expected. However, one can also expect that some substrates will be utilized at higher specific rates than others. Consequently, depending on relative concentrations, one substrate may be effectively removed from the medium before the other. The effects of different removal rates on activated sludge response will be discussed later.

Microbial Product Formation

In chemostat studies of single organism species grown on single substrates the effluent substrate concentration historically was measured for the same compound as that in the influent. For example, if the influent substrate was glucose, glucose was the measured effluent parameter. From the data on concentrations of, say, glucose and micro-organism mass in the effluent, the influent glucose concentration, and the hydraulic retention time in the chemostat, the hypothesized relationships between growth rate and substrate concentration surrounding the organism, such as Monod's, were tested and evaluated.

In the above procedure an error would arise if the effluent specific substrate concentration, converted to COD, is less than the total soluble effluent COD concentration. A number of such observations have been reported in the literature; these are comprehensively reviewed by Daigger and Grady (1977). The phenomenon has been ascribed to microbial product formation.

Grady and his group have studied microbial product formation intensively, both for pure culture/single substrate and mixed culture/single substrate systems (Grady, Harlow and Riesing, 1972).

Using a chemostat at 30°C, they studied the response of pure cultures of A.aerogenes and E.coli with glucose as substrate, and mixed cultures with glucose as substrate. Organism retention times ranged from 5,3 to 11,1 hours. In the effluent from both pure and mixed cultures the glucose COD per se was always less than the total soluble COD. With the pure cultures the effluent glucose COD appeared to conform to prediction based on Monod's specific rate equation, but the total effluent soluble COD did not. In the mixed cultures both the effluent glucose COD and total effluent soluble COD did not conform to Monod-based predictions. In addition, the effluent soluble COD was higher for mixed cultures than for pure cultures.

The results of Grady et al can be briefly commented on insofar as these affect Monod's relationship and their relevance to activated sludge process description. It seems clear from the results that the simplistic equation of Monod does not always correctly describe the rates of transformation of substrates to bacterial mass because of byproduct formation. With soluble COD as parameter the Monod relationship necessarily must be accepted as approximate only, with secondary effects that will remain unquantifiable.

One point is clear from Grady's data: as the organism retention time increases the effluent quality improves, and at an 11 hour retention time the effluent COD, in fact, is very low. From experiments of Dold, Ekama and Marais (1980) using glucose as substrate (measured as COD) with mixed cultures at 20°C, at organism retention times of 2,5 days and greater, under square wave, daily cyclic loading conditions, Monod kinetics appear to apply very accurately; this is reflected not only by the prediction of effluent soluble COD, but also by the accurate predictions of oxygen utilization rate over the whole cycle (see Fig 10 later). With regard to effluent quality the COD was approximately 30 mgCOD/ℓ, and near-constant over the whole cycle. If the effluent quality alone had been used as the primary parameter for modelling it would have been difficult to substantiate Monod kinetics whereas Monod kinetics was strongly supported when both effluent quality and oxygen utilization rate measurements were invoked.

In activated sludge processes, except in the aerated lagoon

process (perhaps), the organism retention time is not likely to be less than one day; with the longer organism retention times the effluent soluble COD concentration therefore can be expected to be so small that for modelling purposes, it can be accepted as zero. Furthermore, the influent concentrations of glucose in the experiments of Grady et al ranged from 500 to 1500 mgCOD/ℓ, and this material solely was responsible for the organism mass generated. In normal municipal unsettled influent sewages, Dold, Ekama and Marais (1980) found that the soluble readily biodegradable COD fraction is approximatly 24 percent of the total biodegradable COD so that even with an unusually high total biodegradable COD of, say, 1000 mgCOD/ℓ the soluble COD will be only about 250 mgCOD/ℓ. In addition, the mass of organisms generated is determined by the total biodegradable COD (1000 mgCOD/ℓ). Consequently, the rate of utilization of the soluble biodegradable COD will be much higher than that indicated by this fraction's concentration, so that the effluent soluble biodegradable COD is unlikely to be of significance in activated sludge processes operated at sludge ages greater than, say, 2 days.

In developing a general model for the activated sludge process Dold et al retained Monod's relationship for determining the kinetic behaviour of soluble readily biodegradable COD, but they determined the magnitudes of the vital constants μ_m and K_s (Eq 2) by calibrating the model using, inter alia, the oxygen utilization rate response instead of the effluent quality. (In sewage, use of the effluent COD quality in any case is not possible because the soluble biodegradable COD cannot be identified directly as the effluent COD contains unbiodegradable soluble material).

In general it would seem that the focus on effluent quality as one of the primary parameters in process kinetic description, and the relative neglect of the oxygen utilization rate, have had a restrictive effect on the development of reliable activated sludge process models. This observation will become even more relevant once the kinetics of particulate biodegradable COD utilization is reviewed later.

MIXED CULTURES

Although pure culture research has provided the basis for much of

the investigation into microbial behaviour, with incalculable benefit to mankind particularly in the medical field, it is true also that "...pure culture growth systems are highly unrepresentative of almost all the habitats that support the growth of microorganisms" (Slater, 1981). Once two or more organisms are together in a space with two or more chemically different substrates, interactions between the organisms and with the substrates may become one of great complexity for which no detailed description is possible. In the activated sludge process, for example, the wide range of organisms and substrate sources makes that the ecosystem is constituted of an extremely complex community of organisms in which symbiosis, mutualism, competition, predation, parasitism, induction, reapression, inhibition, etc., and the abiotic components such as substrate type, dissolved oxygen concentration, temperature, etc. all will affect organism types, numbers and response. With this complexity one may well ask: Is the system amenable to quantitative description? Can the pure culture approach have any relevance?

In an endeavour to find answers to these questions one should take note of Odum's (1971) remark regarding the "levels of organisation": The biotic components range in increasing complexity from genes to cells, organs, organisms, populations and communities. These interacting with the abiotic components give rise to corresponding genetic systems, cell systems, organ systems, organismic systems, population systems and ecosystems, each system constituting a level of organization, the level of organization increasing from the genetic to the ecosystem. Odum states that each level of organization develops unique characteristics, that the study of another level aids the study of a particular level but never can completely explain the phenomena at that level. "In other words not all attributes of a higher level are predictable if we know only the properties of the lower level" (Odum).

A second point that Odum makes is that "...homeostatic mechanisms, that is, checks and balances, forces and counter forces, operate all along the line, a certain amount of integration occurs as smaller units function within larger units. For example, the rate of photosynthesis of a forest community is less variable than that of the individual leaves or trees within the community because as one part slows

down another speeds up in compensatory fashion". Not only does each level of organization require investigation unique to itself with measurements that may differ from those at other levels, but complicating factors in other levels may be of minor importance at the level under consideration and vice versa.

In terms of the discussion above, at the level of organization exemplified by a mixed culture, homeostasis has a balancing effect on the disparate response of the individual organism, to give rise to a lumped mean response as if the organisms can be aggregated into a single (surrogate) organism mass having the observed response characteristics. In this organism mass, detailed consideration of the individual species will have little relevance as homeostatic effects will provide compensatory effects. However, any marked deviations imposed on the system away from the conditions under which it was developed may lead to a response that qualitatively deviates from that normal to the benchmark surrogate mass. Such deviations may appear, for example, when single substrate from an industrial source replaces the mixed substrate from a municipal source, or, where the organism retention time in an experiment is reduced to such a low level that organisms that have a significant effect on the response at long retention times are washed out, causing a qualitative change in the organism mass response.

In accepting a surrogate mass it is important, therefore, to delineate, in some measure, the limits of conditions within which the response can be expected to remain substantially consistent. Such constraints have evolved naturally in the activated sludge process. Three examples can be cited: (1) Theoretical considerations based on experimental evidence has designated lower limits to the sludge ages of plants required to ensure nitrification, the limits being functions of temperature, sewage characteristics and other lesser factors; (2) In anoxic/aerobic operation some experience indicates that the actual duration of an anoxic state at any given time, together with the number of times per day the anoxic state is induced, need to be limited if the denitrification response and sludge settling characteristics are not to be impaired; (3) In anaerobic/aerobic operation, if the anaerobic mass fraction exceeds a certain upper fraction dependant on the temperature and

sludge age, then with municipal influents the particulate components in the influent cannot be metabolized and the system breaks down. This phenomena also is observed in aerobic systems when the sludge age is reduced to below 3/4 to 2 days, depending on temperature (Arkley and Marais, 1981).

Given these introductory remarks we shall attempt to develop the characteristics of the surrogate organism mass, paying particular attention to deviations from, and apparent or real similarities between pure cultures and this surrogate mass and develop a series of models based on the assumed surrogate mass characteristics.

ENDOGENOUS MASS LOSS MODEL

Endogenous Mass Loss

It is in the concept of endogenous mass loss that the first major difference between pure culture and naturally developing mixed cultures becomes a matter of importance. Bhatla and Gaudy (1965), while investigating the BOD-time curve, pasteurized a fraction of the innoculum (to kill protozoa) and thereafter innoculated the pasteurized and unpasteurized innocula, respectively, into a glucose-based substrate. Oxygen consumption and the numbers of bacteria and protozoa were measured over the period of the test (approximately 8 days). The results are shown in Fig 3. The pasteurized culture, after a delay, showed rapid total oxygen uptake over the subsequent 24 hours and thereafter very little additional uptake. The viable bacterial numbers increased concurrently with the oxygen demand and thereafter remained virtually static. With the unpasteurized innoculum the initial total oxygen uptake also was rapid over a period of one day; thereafter it levelled off for a short period, whereupon a secondary phase of oxygen uptake developed over the next six days, almost equal in magnitude to that during the first phase. During the first phase of oxygen uptake the bacterial numbers increased concurrently, to approach a concentration approximately equal to that with the pasteurized innoculum. However, concommitant with the second phase of oxygen demand, the bacterial numbers declined rapidly and the protozoan numbers increased. Evidently the predation of the protozoa on the bacteria was the cause of the second phase of oxygen demand, the bacteria serving as a substrate source for growth of the protozoa so that

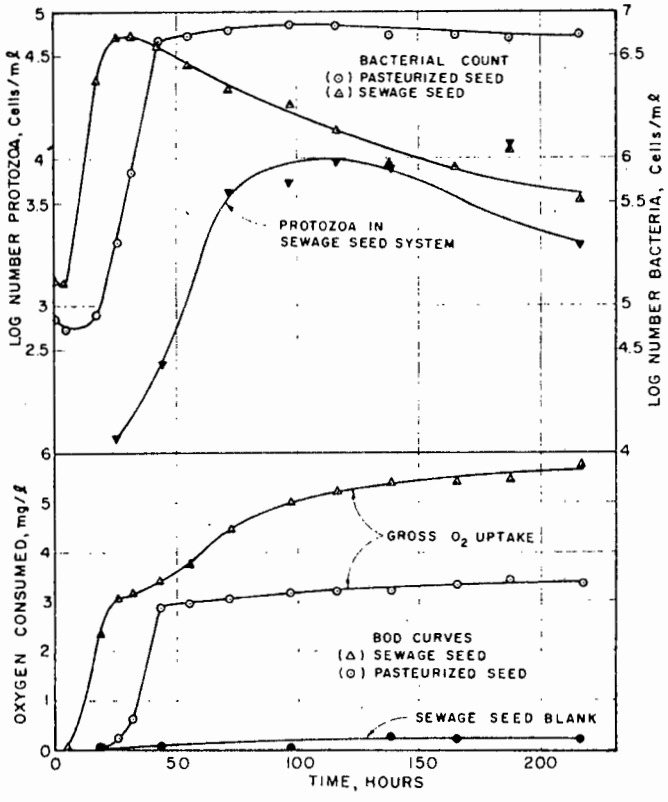

Fig 3 Batch response of pasteurized and unpasteurized mixed cultures with glucose as substrate. Plots of bacterial and protozoan numbers and corresponding cumulative oxygen demands with time indicate effect of predation on oxygen demand (after Bhatla and Gaudy, 1965).

the oxygen uptake probably was principally for synthesis requirements.

Applying the considerations above to mixed cultures in a completely mixed activated sludge process, predation will be a real factor as protozoa form a significant fraction of the microbiological community in the process. The mass of organisms generated will be less than with a pure culture, due to the loss of energy associated with protozoan mass synthesis. Viewed as a surrogate mass, metabolism of the substrate will generate mass as with a pure culture but the predation effect will be apparent as an endogenous mass loss effect.

Although the regulatory aspects in the activated sludge ecosystem at present are beyond quantitative description the global response can be delineated with reasonable reliability. The endogenous mass loss appears to be well-defined relative to the active mass. This is evident in digestion studies of the mass generated in the process: In an aerated mixed liquor sample, if the oxygen utilization rate (OUR) is measured periodically over, say, 10 days, making due correction for nitrification, the plot $\log_e$(OUR) versus time gives rise to a linear relationship (Fig 4). The slope is independent of the sludge age of the process from which the sample was taken, but a function of temperature (Figs 5 and 6). Now the mass of oxygen utilized is associated with an equivalent mass loss, approximately

$$M\Delta O = f_{cv}\, M\Delta X_a \qquad (14)$$

where f_{cv} = COD:VSS ratio (in the range 1,42 to 1,48; Marais and Ekama, 1976).

Hence the slope also describes the specific mass loss rate of the active mass and defines the specific endogenous mass loss rate constant, b, i.e.

$$dX_a/dt = -b\, X_a \qquad (15)$$

Thus, although the causes for the "endogenous" mass loss in the surrogate mass differ fundamentally from those in a pure culture it is still possible to retain the structure of Herbert's model for describing the

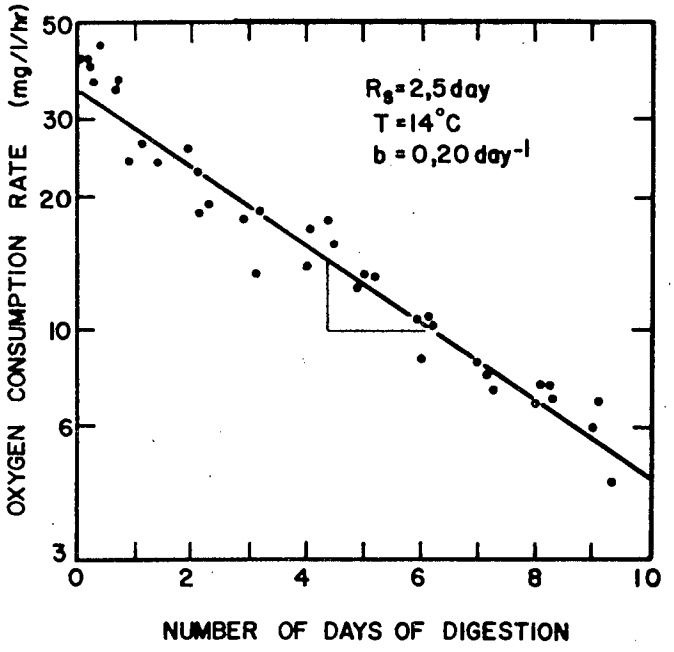

Fig 4 Example of the oxygen utilization rate *versus* time in a batch digestion test of mixed liquor (after Marais and Ekama, 1976).

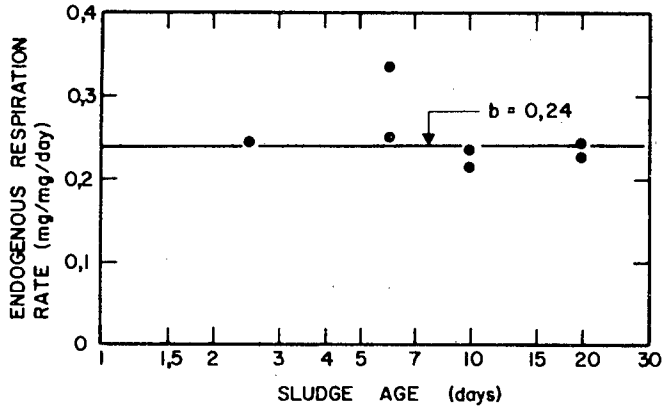

Fig 5 Independency of the specific rate of endogenous oxygen demand from sludge age from oxygen utilization rate *versus* time plots (as in Fig 4) at 20°C (after Marais and Ekama, 1976).

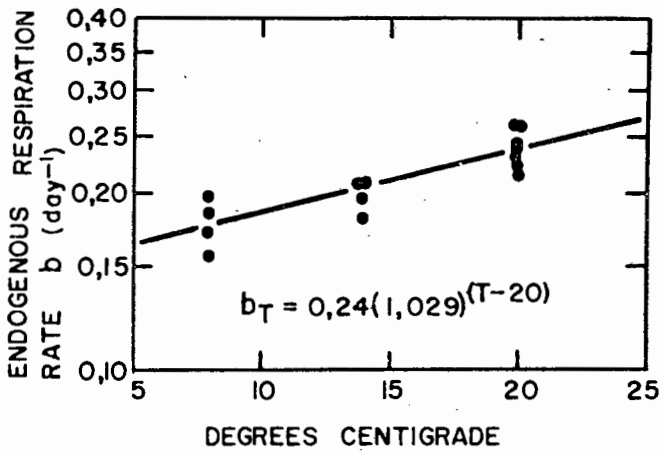

Fig 6 Temperature dependency of specific rate of endogenous oxygen demand (after Marais and Ekama, 1976).

mass loss (Eq 9). However, now one can expect that at sludge ages below which the protozoa are washed out, the specific endogenous mass loss constant will change in magnitude. "True" endogenous mass loss also will occur (if our concept of maintenance is correct) but it seems that this effect is now insignificant compared with the "apparent" endogenous loss as exhibited by the surrogate mass; in any case the loss due to maintenance can be lumped with the prey-predator endogenous loss as both are proportional to the active mass.

Endogenous Residue

The surrogate mass exhibits a further characteristic which has received little attention from pure culture kineticists; namely, The generation of an appreciable inert organic fraction during "endogenous" mass loss, called endogenous residue. The generation of this material has been established beyond doubt (McCarty and Brodersen, 1962; Washington and Hetling, 1965). From these findings, when the active mass per se reduces by one unit, approximately 0,2 units of endogenous residue is generated.

The first explicit incorporation of endogenous residue into an activated sludge process theory was due to McKinney and Ooten (1969). They formulated endogenous residue (X_e) generation as follows:

$$dX_e/dt = 0,2(dX_a/dt)$$
$$= 0,2\ bX_a$$

Basic Equations

Incorporating the endogenous residue relationship, it becomes possible to develop a set of basic relationships that would govern the activated sludge process: Marais and Ekama (1976), in essence following McKinney's proposals (except for his substrate utilization rate equation which they replaced by Monod's), and strongly influenced by the work of Lawrence and McCarty (1970), proposed the following basic relationships:

(a) Synthesis:

$$\left(\frac{dX_a}{d_t}\right)_s = Y\left(\frac{K_m S}{K_s+S}\right)X_a \qquad (15)$$

where $K_m = (\mu_m/Y)$

(b) Endogenous mass loss:

$$\left(\frac{dX_a}{dt}\right)_e = -b\ X_a \qquad (16)$$

(c) Endogenous residue generation:

$$\frac{dX_e}{dt} = 0{,}2\ b\ X_a \qquad (17)$$

(d) Oxygen requirements:

1. Synthesis:

$$\left(\frac{dO}{dt}\right)_s = (1-f_{cv}Y)\left(\frac{dS}{dt}\right)$$

$$= (1-f_{cv}Y)\left(\frac{K_m S}{K_s+S}\right)X_a \qquad (18)$$

2. Endogenous mass loss:

$$\left(\frac{dO}{dt}\right)_e = (1-0{,}2)\ b\ f_{cv}\ X_a$$

$$= 0{,}8\ b\ f_{cv}\ X_a \qquad (19)$$

Steady State Equations

Applied to a completely mixed activated sludge process (CMASP) operated at a sludge age R_s days, and receiving a domestic wastewater, the following equations (in mass terms) were developed:

$$MX_a = \left(\frac{Y \cdot M\Delta S}{1+bR_s}\right)R_s \qquad (20)$$

$$MX_e = 0{,}2\ b\ R_s\ MX_a \quad (21)$$

$$MX_i = MX_{ii} \cdot R_s \quad (22)$$

$$MX_v = MX_a + MX_e + MX_i \quad (23)$$

$$MO/d = (1-f_{cv}Y)M\Delta S = 0{,}8\ b\ f_{cv}\ MX_a \quad (24)$$

where

MX_a = mass of active volatile settleable solids in the process (mgVSS)

MX_e = mass of endogenous residue volatile settleable solids in the process (mgVSS)

MX_i = mass of inert volatile settleable solids (from the influent) accumulated in the process (mgVSS).

MX_{ii} = mass of inert volatile settleable solids entering the process via the influent per day (mgVSS/d)

R_s = sludge age (days)

$M\Delta S$ = mass of biodegradable substrate utilized per day (mgCOD/d)

MO/d = mass of oxygen utilized per day (mgO/d).

The changes in the various fractions with sludge age for a completely biodegradable substrate are shown in Fig 7. It should be noted that in this presentation the biodegradable effluent quality has not been quantified; however, in determining $M\Delta S$ it is assumed that this is duly accounted for. This aspect will be dealt with after examining the chemical constitution of a typical municipal wastewater.

Marais and Ekama (1976) used this approach to study the CMASP

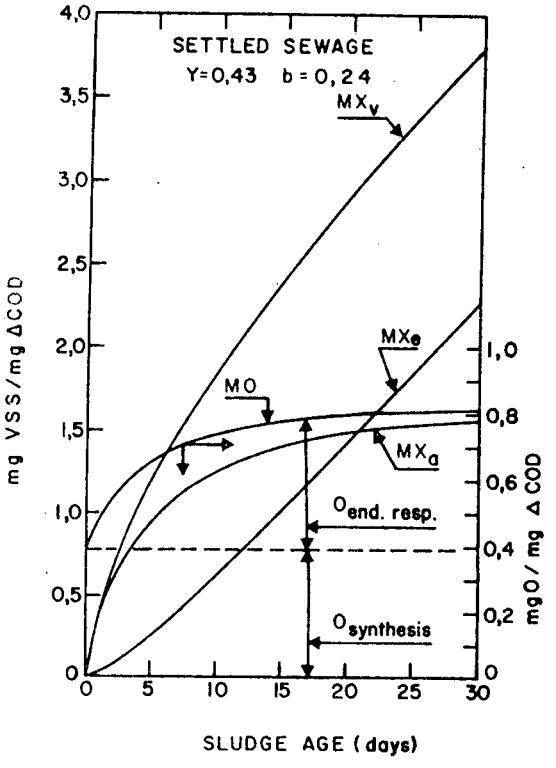

Fig 7 Masses of sludge fractions and daily oxygen demand *versus* sludge age in a reactor for 1 mgCOD utilized per day (after Marais and Ekama, 1976).

under steady state conditions using well-settled sewage in which the inert particulate fraction could be accepted as near-zero. They determined the endogenous mass loss constant, b, by the procedure illustrated in Fig 4 and found that the model gave very good correspondence between the observed and predicted output parameters (total volatile settleable solids concentration, X_v, and carbonaceous oxygen utilization rate) for sludge ages ranging from 2,5 to 30 days if Y was chosen as 0,43 mgVASS/mgCOD.

Furthermore, developing the aerobic digestion aspect, they showed that the theoretical structure allowed the initial active and inert mass fraction of any mixed liquor to be determined either from a series of OUR measurements over a period of time or a series of volatile solids determinations over a period of time. To illustrate, digestion data from Adams, Eckenfelder and Stein (1974) was analyzed in terms of the theory. In Fig 8 the value of b is determined and in Fig 9 the interrelationship between inert, active and endogenous material generated over the period of the test is shown as predicted by the model set out above.

To test the model Eqs (15 to 19) were incorporated in a mathematical model describing the response behaviour of a completely mixed aerobic activated sludge process subjected to dynamic loading conditions. A laboratory unit was operated at a 2,5 day sludge age with a daily cyclic square wave input load (i.e. 12 hours feed, 12 hours no feed) with glucose as substrate. Accepting a K_s value of 40 mgCOD/ℓ and a K_m (μ_m/Y) value of 12 mgVSS/(mgCOD.d), simulated and observed oxygen utilization rate (OUR), total volatile settleable solids and effluent COD concentrations responses are compared in Fig 10; evidently the model appeared to be acceptable for simulating the dynamic process response.

Application of the model above to simulate the response in the same experiment, but using raw sewage as substrate, however, gave predictions completely at variance with observation (see Fig 11). While with glucose the OUR on feed termination decreased precipitously to a value corresponding to the OUR for endogenous respiration, with sewage a small precipitous drop in OUR was evident, whereafter the OUR remained near constant for a period (± 2 hours) after which it decreased gradually until it levelled out at the rate corresponding to endogenous

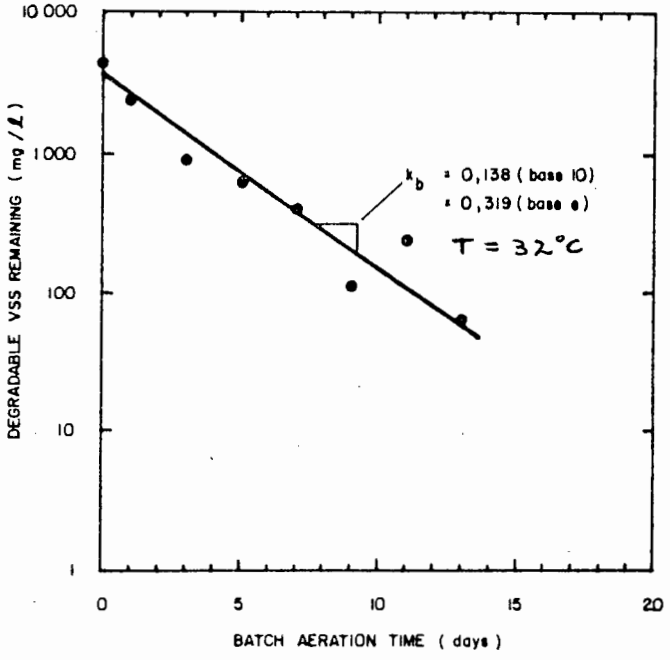

Fig 8 Analysis of digestion volatile solids *versus* time data to determine specific endogenous mass loss rate coefficient, b (Data from Adams et al., 1974; analysis from Warner, Ekama and Marais, 1983).

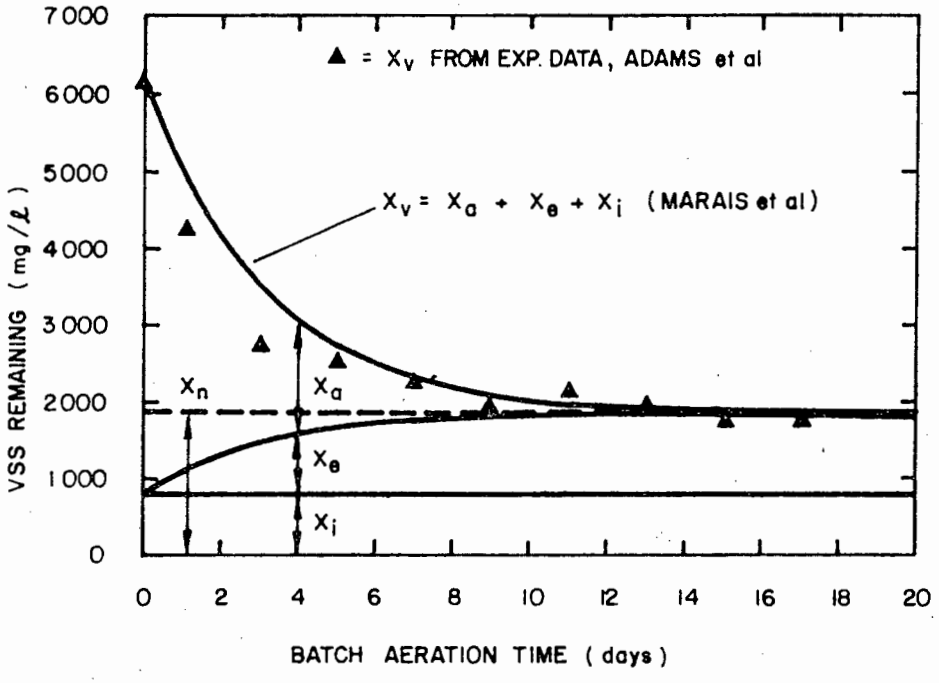

Fig 9 Prediction of active, endogenous and inert volatile solids concentrations for the batch digestion data analyzed in Fig 8 (after Warner et al., 1983).

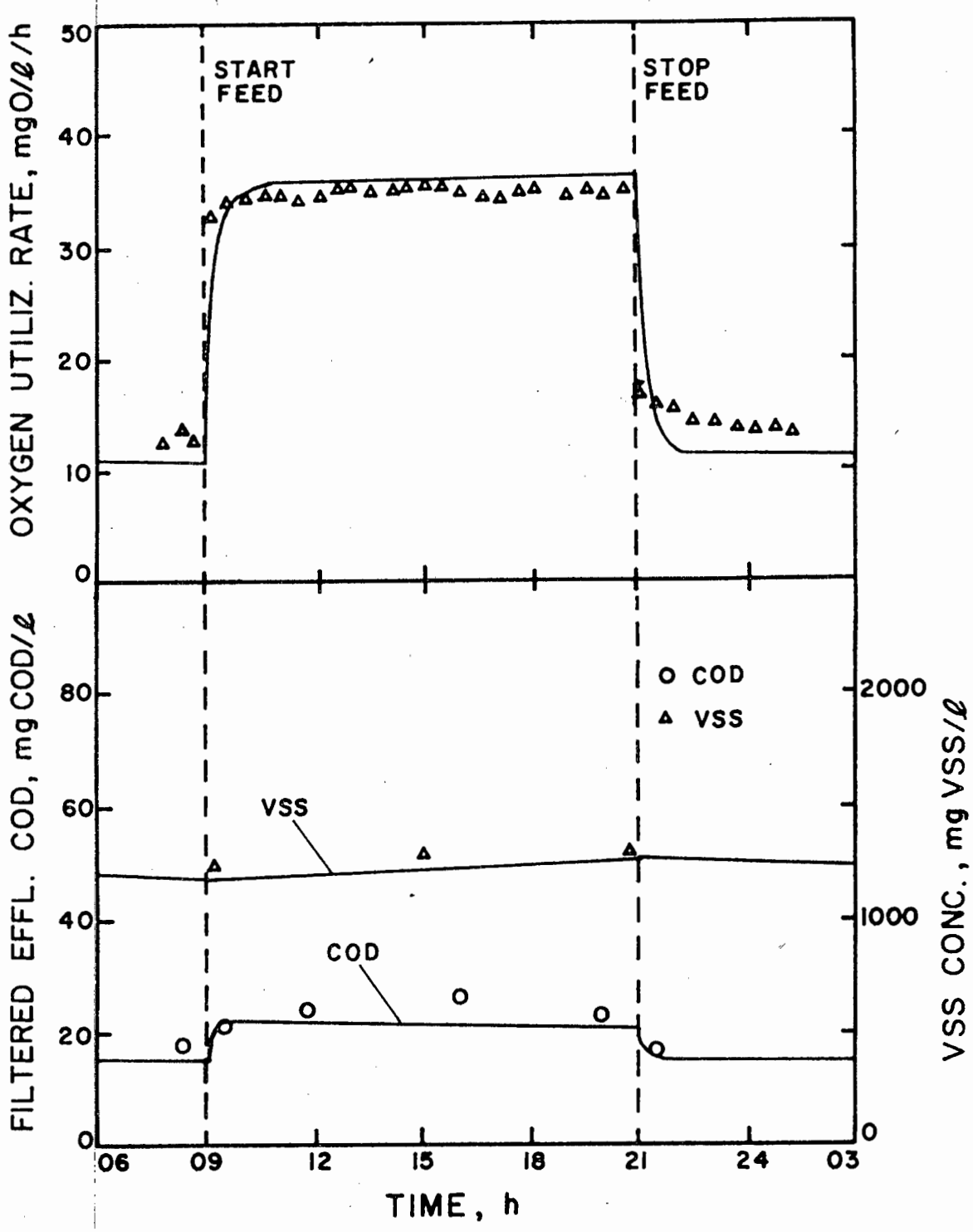

Fig 10 Oxygen utilization rate, volatile settleable solids concentration and filtered effluent COD concentration response in a single reactor CMASP under a cyclic square wave load input (12 hours feed; 12 hours no feed) with glucose as substrate; temp = 20°C.

Predicted response using Monod's specific growth equation.

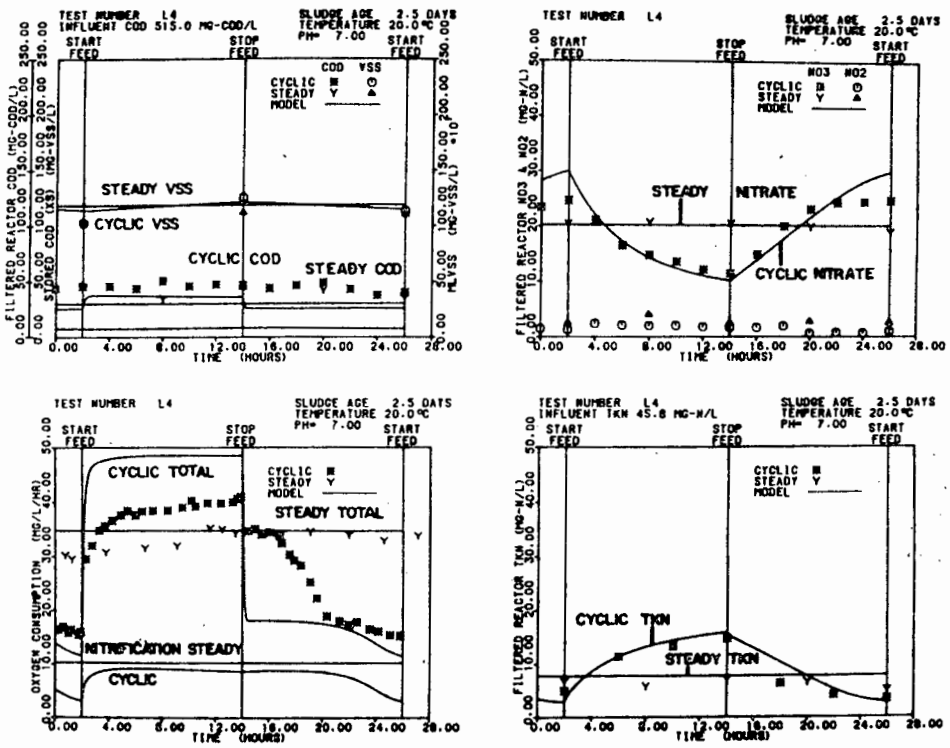

Fig 11 Predicted response using Monod's specific growth rate equation compared to observed response in a single reactor CMASP under square wave daily cyclic loading conditions at 2,5 day sludge age with raw sewage as influent; temp = 20°C (after Dold et al., 1980).

respiration. This qualitative difference in behaviour indicated that a major reappraisal of the process kinetics was necessary in the case with sewage as substrate. This reappraisal involved principally consideration of the substrate constitution in reformulating the substrate utilization rate (or equivalently the organism growth rate) equations.

BISUBSTRATE MODEL

Approximately 60 to 70 percent of the COD in municipal wastewater is in particulate form. The balance is in colloidal and soluble form but even the latter may contain complex organic constituents that cannot be utilized directly by the organism mass. Consequently, the major fraction of the influent COD is unlikely to be metabolized in accordance with Monod's rate equation (Eq 2) as this relationship, as stated before, implies direct utilization of the substrate. For convenience, designate all biodegradable COD fractions that cannot be utilized directly by the term biodegradable particulate COD and all fractions that can be utilized directly as biodegradable soluble COD. The biodegradable particulate fraction will require adsorption onto the organism (i.e. extracellular storage takes place); the stored material then will require to be broken down by hydrolytic enzymes, to smaller molecular units that can pass through the cell wall for utilization by the organism. Adsorption, storage and hydrolytic breakdown therefore need to be considered because, if the rate of adsorption and breakdown takes place at a rate lower than the rate of metabolism of the material derived from breakdown, then the lowest rate will govern the rate of utilization of the particulate substrate.

Andrews and his group were the pioneers in developing a biokinetic theory for describing particulate substrate utilization. In essence this entails two processes, substrate storage and substrate utilization.

Substrate storage: McLellan (1969) demonstrated that there is a maximum level for stored substrate called the available storage potential and that the driving force for substrate storage is dependent on the level of stored substrate - the lower the storage level the faster the storage

rate. Blackwell (1971) considered that both soluble and particulate substrate require to be adsorbed and stored, and proposed that the transfer of substrate from the liquid to the floc may be formulated as follows:

$$\frac{dS_b}{dt} = -K_a S_b X_a \ (f_{ma} - X_s/X_a) \qquad (25)$$

where

K_a = substrate transfer rate (mgCOD/mgVASS/d)

X_a = active volatile solids concentration (mgVASS/ℓ)

S_b = biodegradable substrate concentration in the liquid phase (mgCOD/ℓ)

X_s = stored substrate concentration (mgVSS/ℓ)

f_{ma} = maximum fraction of substrate that can be stored on the active organism mass (mgVSS/mgVASS).

Correspondingly, this gives rise to a storage rate

$$\left(\frac{dX_s}{dt}\right)_{storage} = K_a S_b X_a (f_{ma} - X_s/X_a)/f_{cv} \qquad (26)$$

Adsorption is an example of a mass transfer process and its formulation, as expressed in Eq (25) above, is in conformity with mass transfer principles.

Andrews and Busby (1973) suggested that Blackwell's equation was deficient in that it did not consider the effect of substrate concentration in the liquid phase and proposed that f_{ma} be modified to give:

$$\frac{dS_b}{dt} = -K_a S_b X_a \left(f_{ma}\left(\frac{S_b}{K_s+S_b}\right) - X_s/X_a\right) \qquad (27)$$

They justified this modification by noting that Morris and Stumm (1960) found that adsorption of substrate was dependent on the substrate concentration in the liquid phase. However, it is doubtful whether the modification reflects this as it merely introduces a variable storage potential. In the absence of definitive evidence supporting Andrews and Busby's modification the equation of Blackwell can be accepted.

Stored substrate utilization: The mass of stored substrate is determined from the difference between the rate of adsorption and the rate of hydrolytic breakdown. Noting how rapidly biodegradable soluble COD is utilized, the process of hydrolytic breakdown and utilization of the products can be formulated as a single rate equation, that defining the rate of hydrolytic breakdown.

The rate of stored substrate utilization was formulated by Blackwell (1971), Jacquart, Lefort and Rovel (1973) and Andrews and Busby (1973) as a Monod-type saturation equation of the form

$$\left(\frac{dX_s}{dt}\right)_{syn} = \left(\frac{K_m X_s f_{cv}}{K_s + X_s f_{cv}}\right) X_a \tag{28}$$

$$\text{i.e. } \frac{dX_a}{dt} = Y \left(\frac{K_m X_s f_{cv}}{K_x + X_s f_{cv}}\right) X_a \tag{29}$$

and overall

$$\frac{dX_s}{dt} = \left(\frac{dX_s}{dt}\right)_{storage} - \left(\frac{dX_s}{dt}\right)_{syn} \tag{30}$$

From the work of Porges, Jasewicz and Hoover (1956), f_{ma} appears to have a value approximately unity. Consequently, when X_a is low X_s necessarily is low also, and from Eq (29) the rate of synthesis also will be low. This is contrary to expectation for in such a situation the specific growth rate should be close to the maximum because X_s is large

relative to X_a. This deficiency stems from defining the stored substrate concentration in units relative to the bulk liquid. The difficulty can be resolved by defining X_s relative to the active mass concentration, X_a; that is, the specific rate of utilization is determined by (X_s/X_a) rather than by the bulk concentration, X_s. Consequently Eq (29) should be reformulated as

$$\frac{dX_a}{dt} = Y\left(\frac{K_{mp}(X_s/X_a)}{(K_{sp}/f_{cv}) + (X_s/X_a)}\right)X_a \qquad (31)$$

Stenstrom (1975) developed Eq (31), but in terms of the total volatile solids concentration, X_v, instead of the active volatile solids concentration i.e. (X_s/X_v) instead of (X_s/X_a).

Dold, Ekama and Marais (1980) showed that Eq (31) could be developed from the basis of Levenspiel's (1972) surface reaction theory. This provides a rational basis for Eq 31 to place it on the same semi-empirical footing as Monod's - both have a history of pure empiricism in their initial formulation.

Incorporating the storage approach in the CMASP model appeared to explain the observed oxygen utilization rate (OUR) behaviour subsequent to feed termination in the square wave tests (see Fig 12). However, it did not explain the small precipitous drop in OUR on feed termination. In attempting to explain this latter behaviour, Ekama and Marais (1978) proposed that the adsorption of substrate required energy (or equivalently an oxygen demand), and at feed termination this energy demand ceased, manifesting itself by a precipitous drop in the OUR. Dold, Ekama and Marais (1980) found this argument unconvincing as an adsorbed state should correspond to a lower energy level than the unadsorbed state. Noting the precipitous drop in OUR on feed termination when the soluble substrate glucose served as influent (see Fig 10), they hypothesized that the small precipitous drop when sewage served as influent could be ascribed to a fraction of the sewage having characteristics similar to glucose, and giving rise to a similar response on feed termination. Accordingly, Dold et al. (1980) formulated a bisubstrate model for the activated sludge process in which the overall growth rate was assumed to be equal to the sum of the growth rates of the particulate biodegradable and soluble

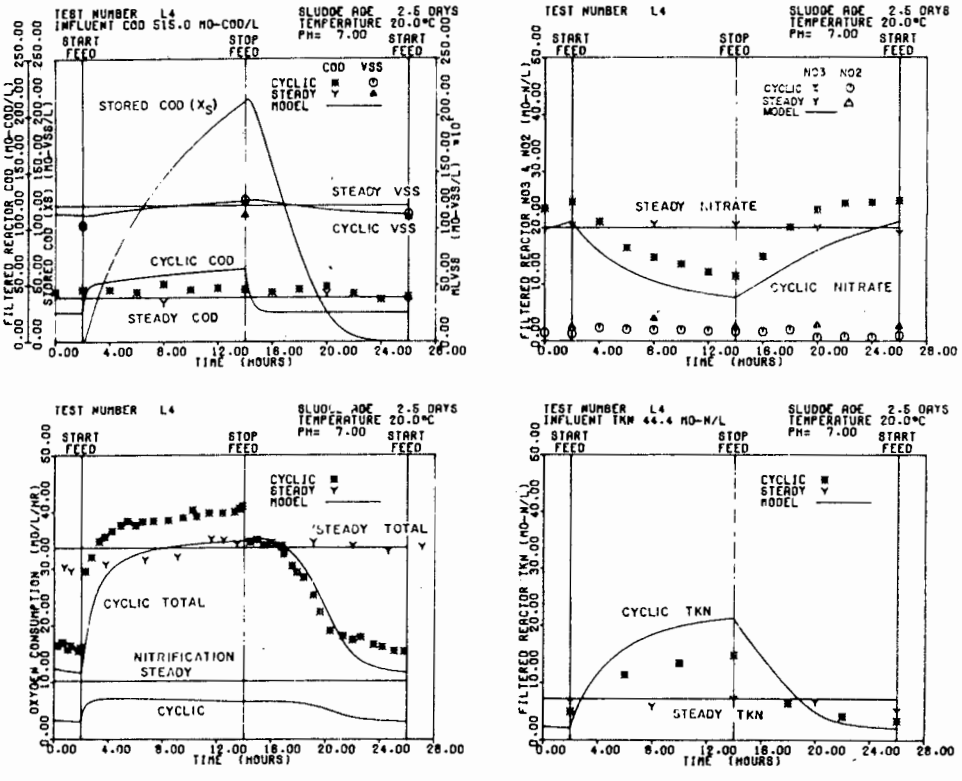

Fig 12 Predicted response of same process as in Fig 11, but assuming all the substrate is stored and the utilization rate of stored material is in accordance with Eq (31) in text (after Dold et al., 1979).

readily biodegradable COD fractions each rate operating independently of the other. The soluble COD was utilized in accordance with Monod kinetics (Eq 2) and the particulate COD in accordance with Levenspiel kinetics (Eq 31). Using this approach Dold et al. were able to simulate very satisfactorily the observed response in the square wave test with sewage as influent (Fig 13).

The model has been used very successfully to simulate the response observed in a range of aerobic CMAS process types: single reactor (operated over a range of sludge ages and temperatures); series reactor; contact stabilization; and aerobic digestion (see Figs 13 to 17).

These simulations were done using the same set of kinetic constants, except for the value of K_{ms} $(=\mu_m/Y)$ in the contact stabilization process where it was required to be reduced. This inconsistency raised the question as to whether the two rates, as assumed in the model, were in fact independent under the high load conditions (high F/M) in the contact reactor. We will return to this question later.

Influent Constitution

Activated sludge process models based on the fundamental biokinetic relationships evolved in terms of the surrogate mass approach provided the structure for determining the various influent substrate components and the biokinetic constants. Differentiation between the various substrate components, and the kinetic response of the process to these, appears to give a rational explanation of much of the observed behaviour.

The division of the influent COD in a sense was determined by the structure of the model. This demanded differentiating between (readily) biodegradable soluble COD (S_{bs}), (slowly) biodegradable particulate COD (S_{bp}), unbiodegradable soluble COD (S_{us}) and unbiodegradable particulate COD ($S_{up} = X_{ii} \cdot f_{cv}$) in the wastewater. In the final analysis these fractions only could be evaluated from the kinetic response of the process; the values find acceptance from the consistency of the response over a wide range of process types and conditions. Figure 18, below,

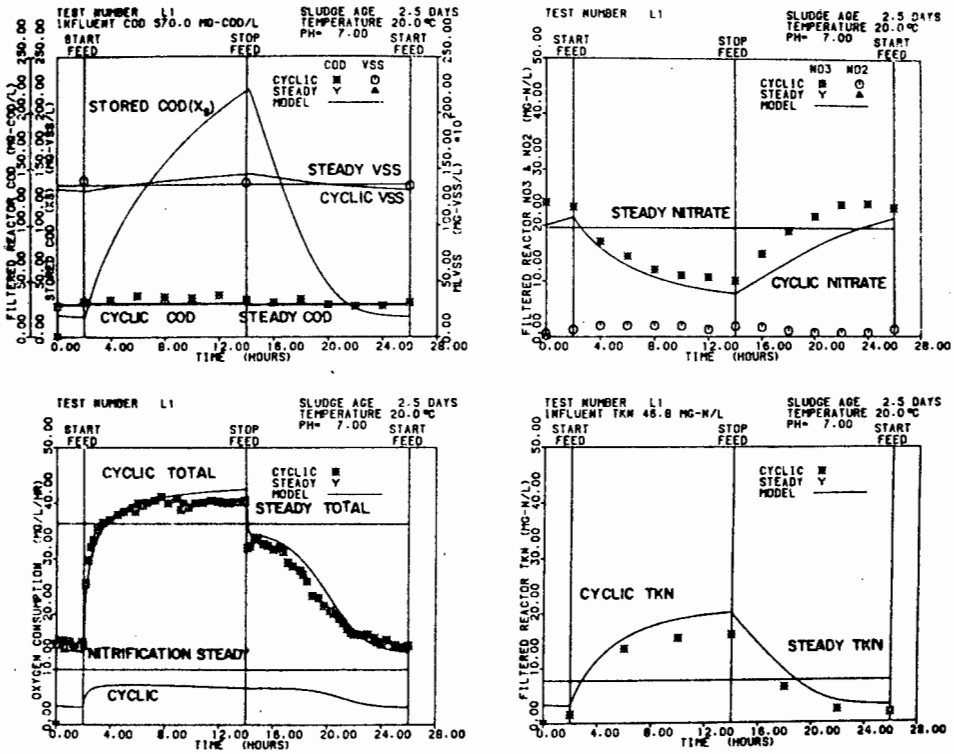

Fig 13 Predicted response of same process as in Fig 11, but accepting a bisubstrate composition of the biodegradable influent COD with readily biodegradable soluble COD utilized according to Monod kinetics and slowly biodegradable particulate COD utilized according to Eq (31) via storage (after Dold et al., 1980).

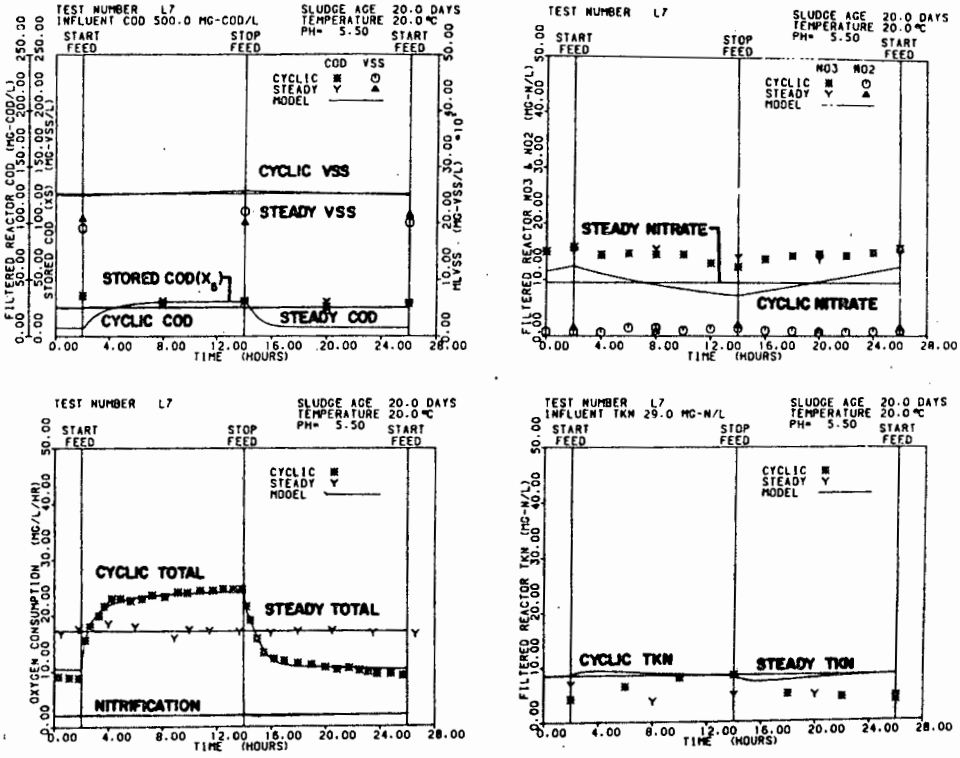

Fig 14 Predicted response using the bisubstrate theory compared to observed response in a single reactor CMASP under square wave daily cyclic loading conditions at 20 day sludge age with raw sewage as influent; temp = 20°C (after Dold et al., 1980).

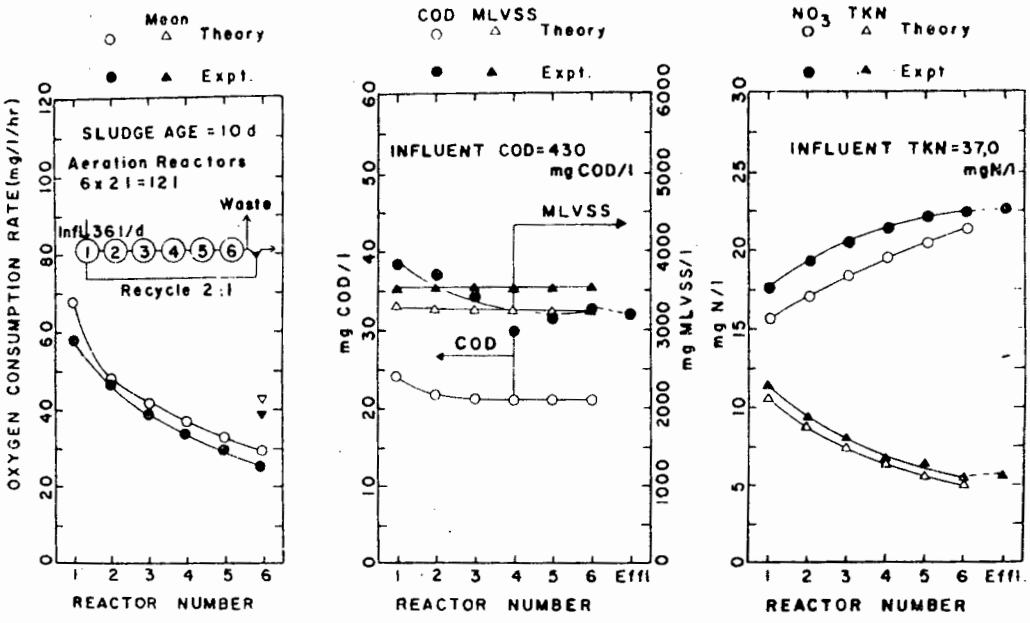

Fig 15 Predicted response using the bisubstrate theory compared to observed response in a series reactor CMASP configuration under steady state loading conditions at 10 day sludge age with raw sewage as influent; temp = 20°C (after Dold et al., 1980).

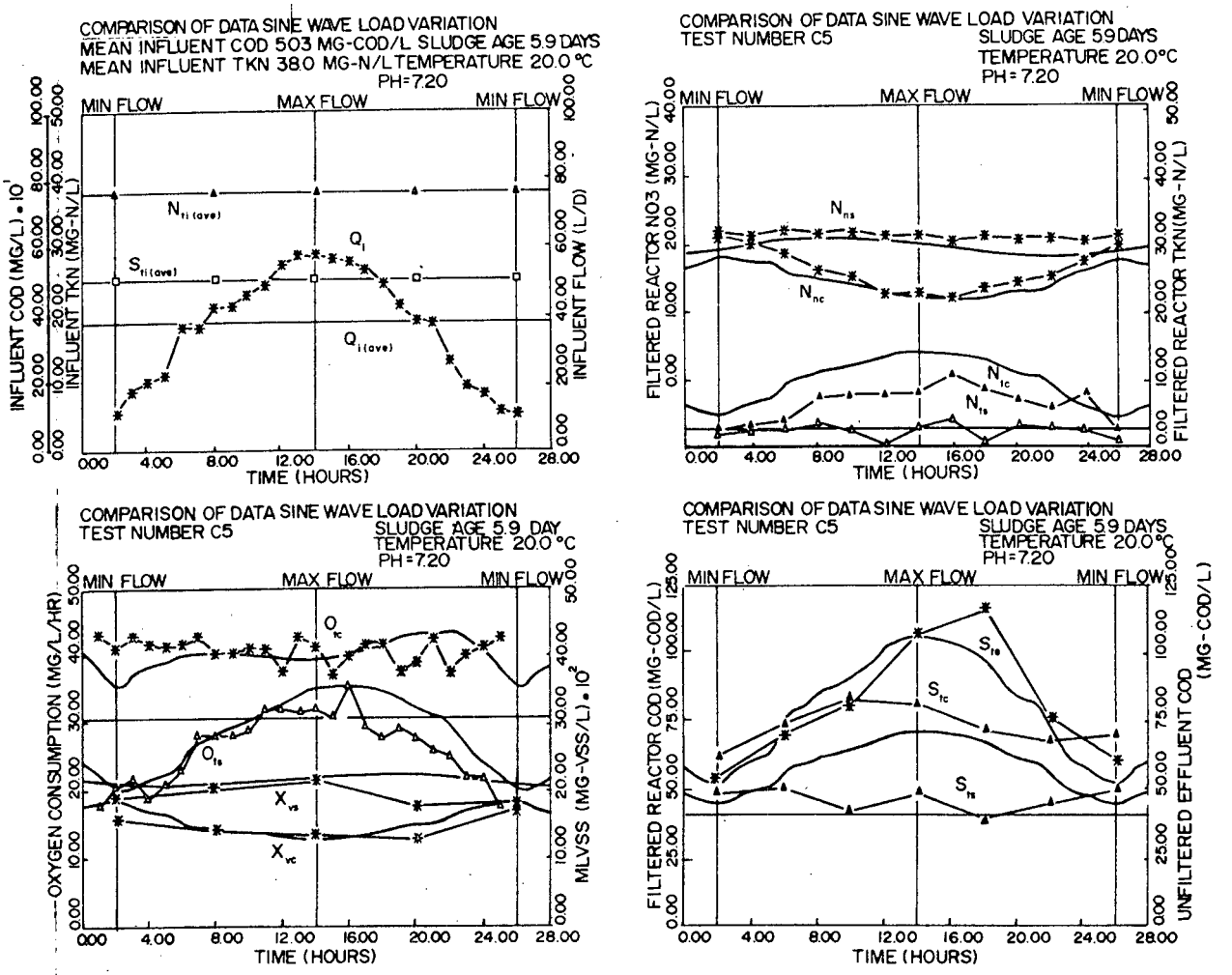

Fig 16 Predicted response using the bisubstrate theory compared to observed response in a contact stabilization CMASP under sine wave daily cyclic loading conditions at 5,8 day sludge age with raw sewage as influent; temp = 19,5°C (after Alexander, Ekama and Marais, 1980).

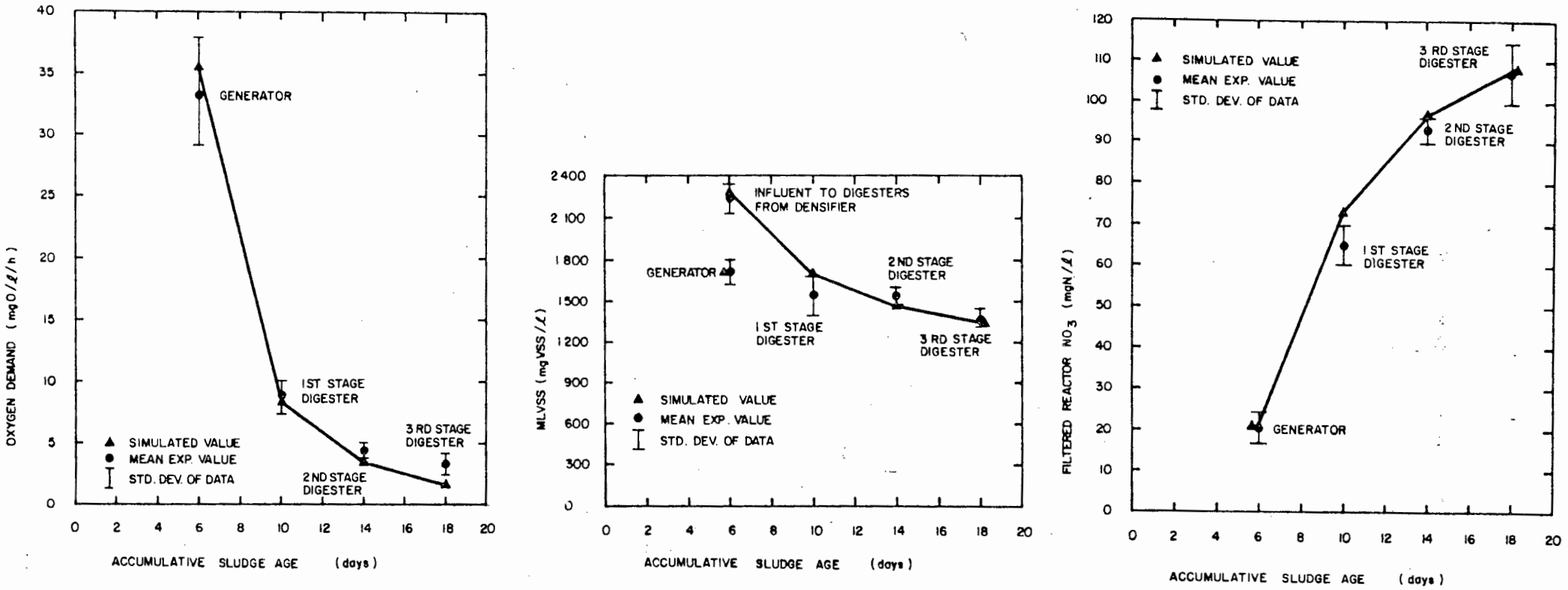

Fig 17 Predicted response using the bisubstrate theory compared to observed response in an activated sludge CMASP receiving raw sewage as influent (6 day sludge age) wasting to three digesters in series, each at 4 day sludge age; temp = 20°C (after Warner et al., 1983).

illustrates the division of wastewater COD into the various components; values in brackets are typical of the magnitudes encountered for an unsettled municipal wastewater from a South African source. (These characteristics are for urban areas where garbage grinding is not practised).

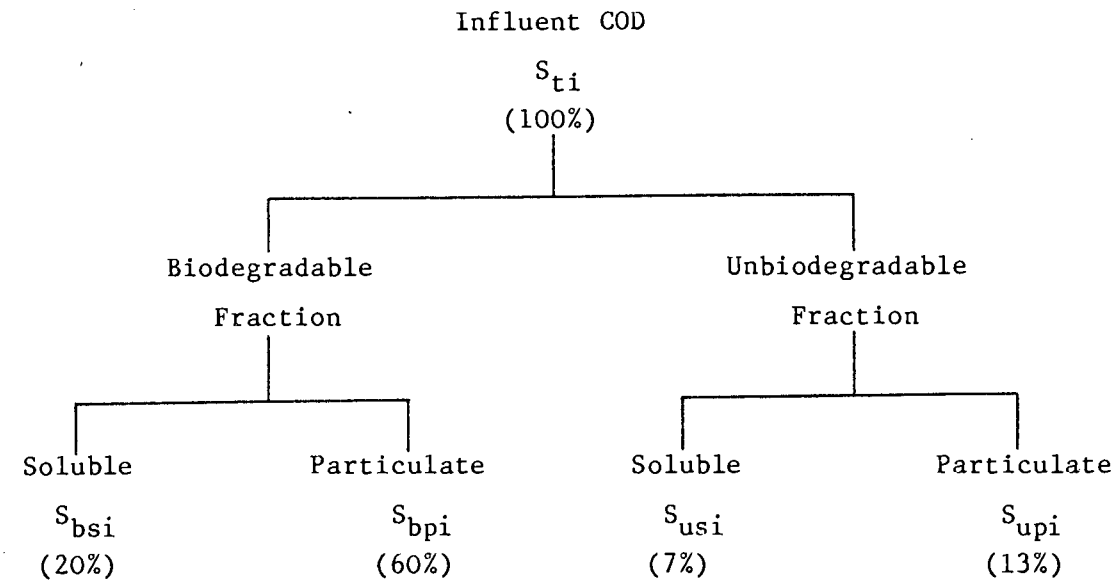

Fig 18: Division of domestic wastewater COD fractions. (Values in brackets correspond to typical magnitudes encountered for South African wastewaters).

Effluent Quality

The organism mass is generated from the total biodegradable influent COD utilized. The unbiodegradable particulate fraction, S_{up}, is enmeshed in the sludge mass and removed via the sludge wastage stream. The biodegradable particulate material is enmeshed, adsorbed and synthesized into organism mass. Therefore, neither of the two particulate fractions appear in the effluent COD. The soluble biodegradable COD is metabolized directly by the organisms; any undegraded biodegradable soluble COD appears in the effluent. The unbiodegradable soluble COD is hypothesized to pass, unaffected, through the process and appears in the effluent.

Experimental observations on processes operated concurrently on the same influent sewage show no difference in effluent COD concentration irrespective of sludge age and loading pattern, provided the sludge age is greater than 2 to 3 days. This insensitivity of the effluent quality arises from three sources:

(1) The sludge mass is generated from the total biodegradable COD (soluble plus particulate);

(2) The particulate COD does not contribute; and

(3) The specific rate of soluble COD utilization is high.

Given the above factors, in domestic wastewaters the ratio of soluble COD to total active organism mass ("soluble F/total M") generally is very low; as a consequence the biodegradable soluble COD concentration is very low (effectively zero) for sludge ages greater than 2 to 3 days, even under dynamic loading conditions. Therefore the effluent quality is determined solely by the concentration of unbiodegradable soluble COD in the influent (S_{usi}) - from the fact that the effluent COD does not increase with sludge ages from 3 to 30 days it is concluded that none is generated by the process and is derived totally from the influent.

The effect of sludge age on the behavioural pattern is illustrated by simulating the response characteristics of an aerated lagoon over a range of sludge ages from 0,5 to 5 days (Fig 19). In the figure the soluble biodegradable effluent COD concentration, S_{bs}, is virtually zero for sludge ages greater than one day and the stored COD concentration, X_s, becomes effectively zero for sludge ages greater than 2 days. Consequently one can accept that for sludge ages greater than 2 days there will be no soluble biodegradable material in the effluent and the particulate biodegradable material is completely metablized. For design purposes, therefore, if $R_s > 2$ days the effluent biodegradable COD can be taken as zero, and the sludge masses generated and oxygen utilized can be determined from the steady state equations (Eqs 20 to 24) assuming complete utilization of all the biodegradable substrate. Using these

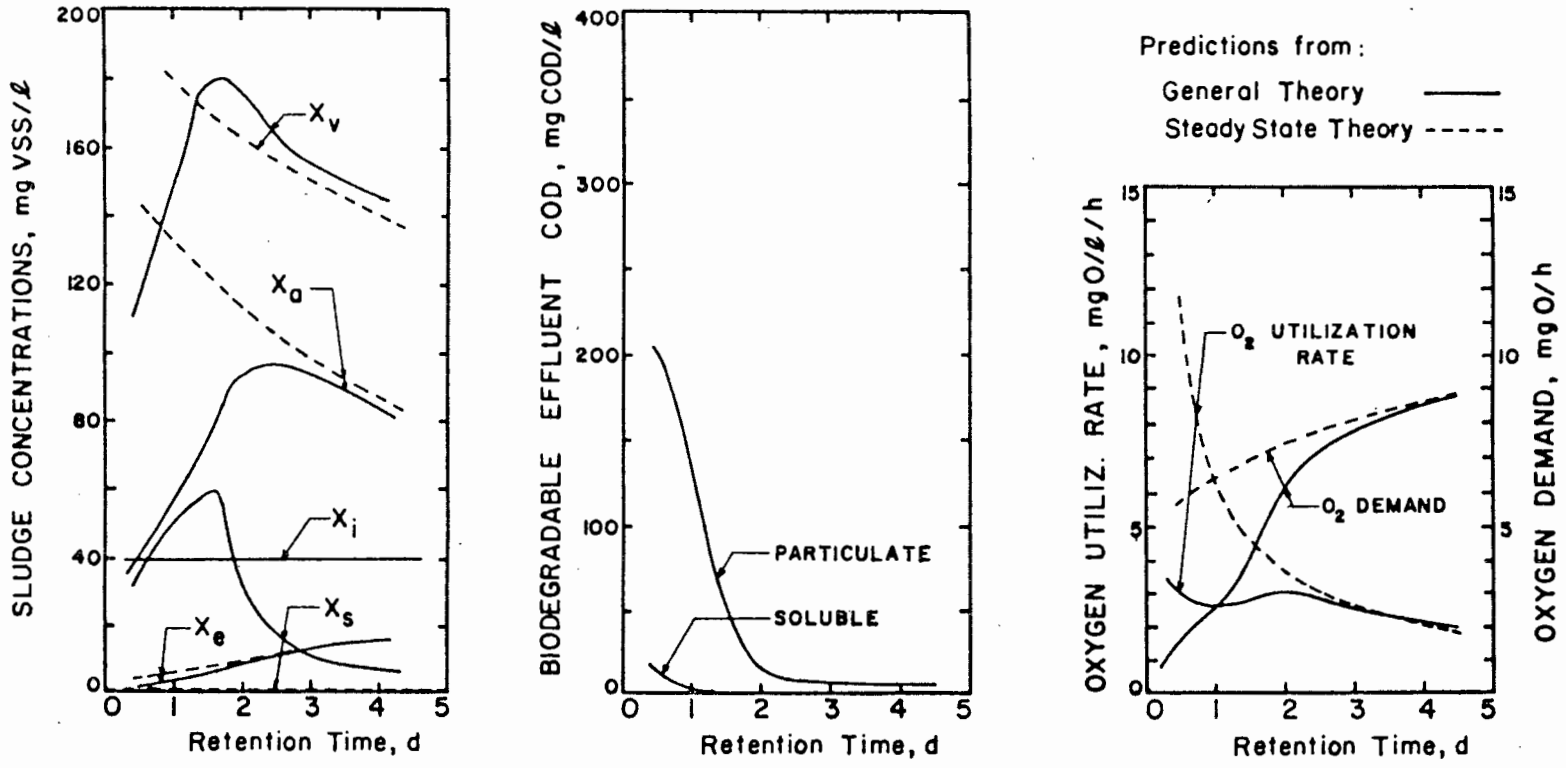

Fig 19 Comparison of predicted response for a suspension mixed aerated lagoon receiving raw sewage for retention times (sludge ages) from 0,5 to 5 days using the bisubstrate general theory and the steady state model; temp = 16°C.

assumptions, the predictions of the steady state equations are superimposed in Fig 19. Evidently, at sludge ages less than 2 days the response characteristics can be estimated theoretically only via the general bisubstrate model.

K_s for Soluble Substrate Utilization

With municipal wastewaters, in order to obtain agreement between observation and simulation using the general model, the half saturation constant for the soluble substrate had to be accepted as approximately 4 to 8 mgCOD/ℓ, whereas K_s values of 80 to 120 mgCOD/ℓ (for sludge ages of about 4 hours) and 20 to 40 mgCOD/ℓ (for sludge ages of about 3 days) are required to simulate the response with glucose as influent. The necessity for this reduction cannot be explained unequivocably, but does find rationality in the quote of Monod earlier in this paper; he indicated that, where a web of enzymes have an influence on the rate, generally K_s will be smaller than if only one of the enzymes controlled the reaction. The smallness of K_s finds verification in batch tests on mixed liquor to which is added a slug of domestic waste. The initial phase of oxygen reduction which is associated with the readily biodegradable COD always is linear until that substrate fraction has been fully utilized, whereupon abruptly the rate changes to a lower value, i.e. due to the low K_s value the rate is zero order down to low soluble substrate concentrations. If K_s were high the simulation indicates that a curved oxygen-time profile would be observed under this condition. This behavioural pattern serves as a cautionary note not to extrapolate, uncritically, single substrate behavioural patterns to complex mixed substrate conditions.

Oxygen Utilization Rate (OUR)

The oxygen utilization rate gives a direct reflection of the metabolic activity of the sludge. Therefore, OUR is a parameter of crucial importance in any kinetic analysis of process behaviour. In this regard the different reactions can be identified only under dynamic conditions; for example, imposing a square wave loading condition. Under steady state conditions the different kinetic reactions cannot be

separated as the overall rate will be that of the rate-controlling step.

Another important aspect of process model development is that process identification is more explicit at short rather than at long sludge ages. At long sludge ages, because most of the reactions are essentially complete, the response of the process tends to follow the influent load pattern. This is illustrated by comparing the OUR response in square wave tests at sludge ages of 2,5 and 20 days, respectively, in Figs 13 and 14. In contrast, the complete insensitivity of the effluent quality to the input load pattern makes that the effluent quality has little value as a basic parameter for model development.

DEATH-REGENERATION MODEL

The concepts, of an endogenous mass loss to describe the prey-predator interaction and the bisubstrate division of the influent, we have seen, allowed a model to be developed that gave good predictions of the response of activated sludge processes under aerobic conditions. However, when the model was applied to systems that included anoxic zones (with nitrate as the only electron acceptor) and/or anaerobic zones (free of both oxygen and nitrate) the response observed deviated from that predicted by the model.

Observations, for example, indicated that (1) inclusion of an anaerobic reactor in an activated sludge process did not affect the endogenous mass loss of the system when compared to an aerobic one operated at the same sludge age; and (2) in an aerobic reactor following an anaerobic one, the oxygen demand was higher by an amount corresponding to that which would have been ascribed to mass loss in the anaerobic reactor had that reactor been aerated (for example, see Fig 24, later).

The qualities assigned to the surrogate mass (which we have shown is based on a prey-predator interaction) in effect lumps the interactive effects as an endogenous mass loss. By ascribing an endogenous mass loss property to the surrogate mass one necessarily also must accept the necessity for an external electron acceptor to obtain the mass loss effect. In the situation where an electron acceptor is not available the mass loss cannot occur, but the model based on the endogenous mass loss concept gives no directive whereby logically the cessation in mass loss

can be compensated for by an above-normal increase in mass loss in a subsequent aerobic state. However, we can assign qualities to the surrogate mass, still based on the prey-predator concept, that do allow the effect of anoxic/anaerobic states to be incorporated consistently into the aerobic activated sludge model.

In the surrogate mass one cannot distinguish between the prey and the predators, but one can describe the predation as a death within the mass and the associated growth of the predators as a synthesis. It is also possible to conceive that (1) the predators themselves do not utilize all the substrate derived from the prey and/or (2) the prey anabolic action produces by-products which in turn stimulate bacterial growth. Viewed as an ecosystem, apparently a stable interactive state between prey and predators is attained. Accordingly, one can assign a global death-regeneration property to the surrogate mass. During an anaerobic phase predation can continue, but utilization of this material cannot take place due to a lack of an electron acceptor. In this phase, therefore, an accumulation of substrate takes place. Subsequently, an aeration, the accumulated substrate material will induce a higher than normal oxygen demand for synthesizing protoplasmic mass. Thus, in the surrogate death-regeneration model we hypothesize a rate of death of the organism mass (a process that continues irrespective of the availability of an electron acceptor) and growth (regeneration) using the dead material as substrate. As there is always a loss of energy (equivalently organic mass) during synthesis, the net effect of the death/growth cycle is a reduction in mass - the endogenous mass loss of the previous model. If the mass receives an external source of substrate the total amount of substrate available to the organism will be that derived from "death" plus that from the outside source.

Viewed from a wider perspective, the death-regeneration approach can be justified without invoking the prey-predation concept. One should remember that an activated sludge process operated at, say, a 20 day sludge age, receives only 5 percent of the substrate per unit organism mass compared to a process operated at, say, a 1 day sludge age (assuming no endogenous mass loss occurs). Bacteria can replicate, in fact, in one to three hours if sufficient substrate is available; consequently, with a

20 day sludge age, even though the mass receives substrate, the organisms are still in a state of extreme nutrient deficiency. Under these conditions it is not unreasonable to speculate that a fraction of the organisms will succumb, release substrate, and the released substrate provide nutrition for the balance. This point of view will suffice also for pure cultures. However, one should note that in Fig 3, the mass loss in a culture without predators was exceedingly small, indicating that the stress induced by a lack of maintenance energy per se is small, resulting in a low death rate. Evidently the small amount of energy thus released is sufficient to maintain vitality in the rest of the organism mass. In contrast, in mixed cultures the predation and other interactive effects causes a high death rate, far greater in intensity than that induced by loss of vitality of the organisms. In mixed cultures, therefore, it would seem that the maintenance function per se is of minor significance, whereas death due to other causes is of major importance. The energy now supports an ecosystem, a community of interactive organisms which apparently requires a much greater throughput of energy, external or self-generated.

Translation of the speculations above into a quantitative theory was relatively easy to accomplish. Quantitative kinetic formulations are detailed by Dold, Ekama and Marais (1980), and there is little point in repeating these here. It suffices to say that the Monod and Levenspiel rate equations for growth on the two respective biodegradable substrate components were retained, but the endogenous mas loss rate approach was replaced by the death-regeneration approach, assuming a constant specific death rate; the biodegradable organic material released on death needed to be formulated as consisting of particulate (slowly) biodegradable substrate - this does not appear unreasonable as the material will be comprised of complex molecules. The biokinetic constants had to be changed appropriately but this was readily accomplished as the endogenous mass loss approach is linearly related to the death-regeneration one.

Simulation using the death-regeneration model has shown that in aerobic systems both theories predict dynamic process response that are virtually identical. Under anaerobic/anoxic/aerobic operation, however, the death regeneration model is superior because it provides for substrate

accumulation during the anaerobic-anoxic phases. By accepting the death-regeneration model it has been possible at the University of Cape Town to simulate, very accurately, the complete spectrum of activated sludge processes so far investigated: these include, besides the aerobic processes described earlier, multi-reactor series processes incorporating anoxic and aerobic zones under cyclic loading conditions (see Figs 20 and 21); sequential anoxic/aerobic states imposed on a single reactor under cyclic and steady state loading conditions (see Figs 22 and 23); and sequential anoxic/aerobic operation of digestors receiving a slug of waste activated sludge once a day (see Fig 24).

The examples above reflect the observed responses of the different processes. There are, however, certain interesting aspects not directly apparent from the results, and these merit comment:

(1) In terms of the death-regeneration model, each day 62 percent of the surrogate mass "dies", the biodegradable mass fraction thus released providing organic energy for the regeneration of 45 percent of that mass fraction as "new" live mass, to give rise to a net specific reduction of 24 percent per day - the same as in the endogenous mass loss model.

(2) The inert fraction of the organism mass (which accumulates as inert endogenous residue on death) comes out to be 8 percent, instead of the 20 percent in the endogenous mass loss model. Due to the large internal recycling of energy the net cumulative effect is an apparent 20 percent inert fraction relative to the 24 percent per day net reduction of active mass. Subjectively, an inert fraction of 8 percent for a microorganism is more satisfactory than 20 percent; the latter seems unreasonably high for a bacterium.

(3) As the operating sludge age is increased the energy recycled in the system due to death becomes the dominating fraction of the total energy processed by the active mass. Speculatively one could wonder if the complex structure of the activated sludge ecosystem and its relatively stable global response is not perhaps a result of the

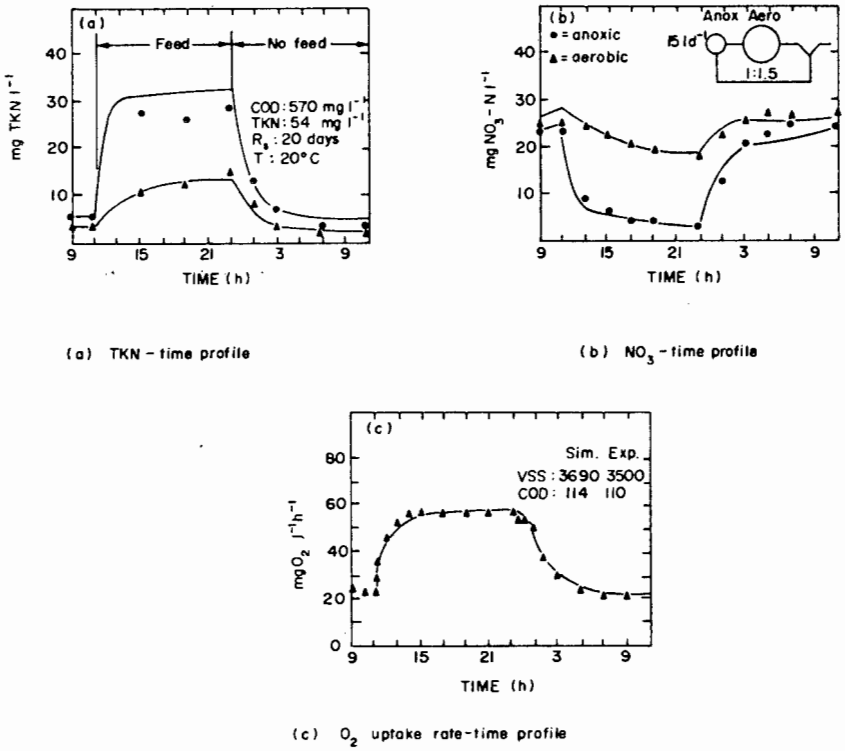

Fig 20 Predicted response using the bisubstrate death-regeneration model compared to observed response in a series reactor CMASP anoxic/aerobic system under square wave daily cyclic loading conditions with raw sewage as influent at 20 day sludge age; temp = 20°C (after van Haandel, Ekama and Marais, 1981).

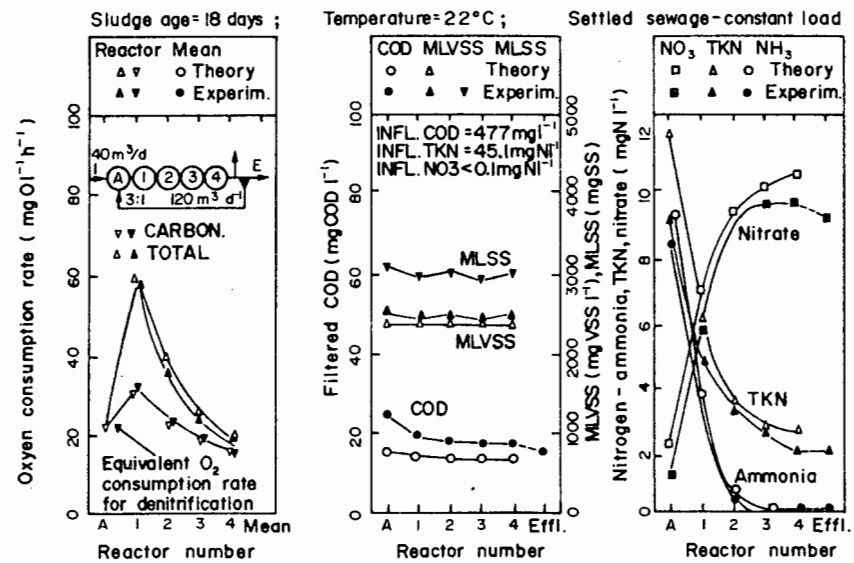

Fig 21 Predicted response using the bisubstrate death-regeneration model compared to observed response in a five reactor series CMASP system with the first reactor unaerated, under steady state loading conditions with settled sewage as influent at 18 day sludge age; temp = 20°C (after van Haandel et al., 1981).

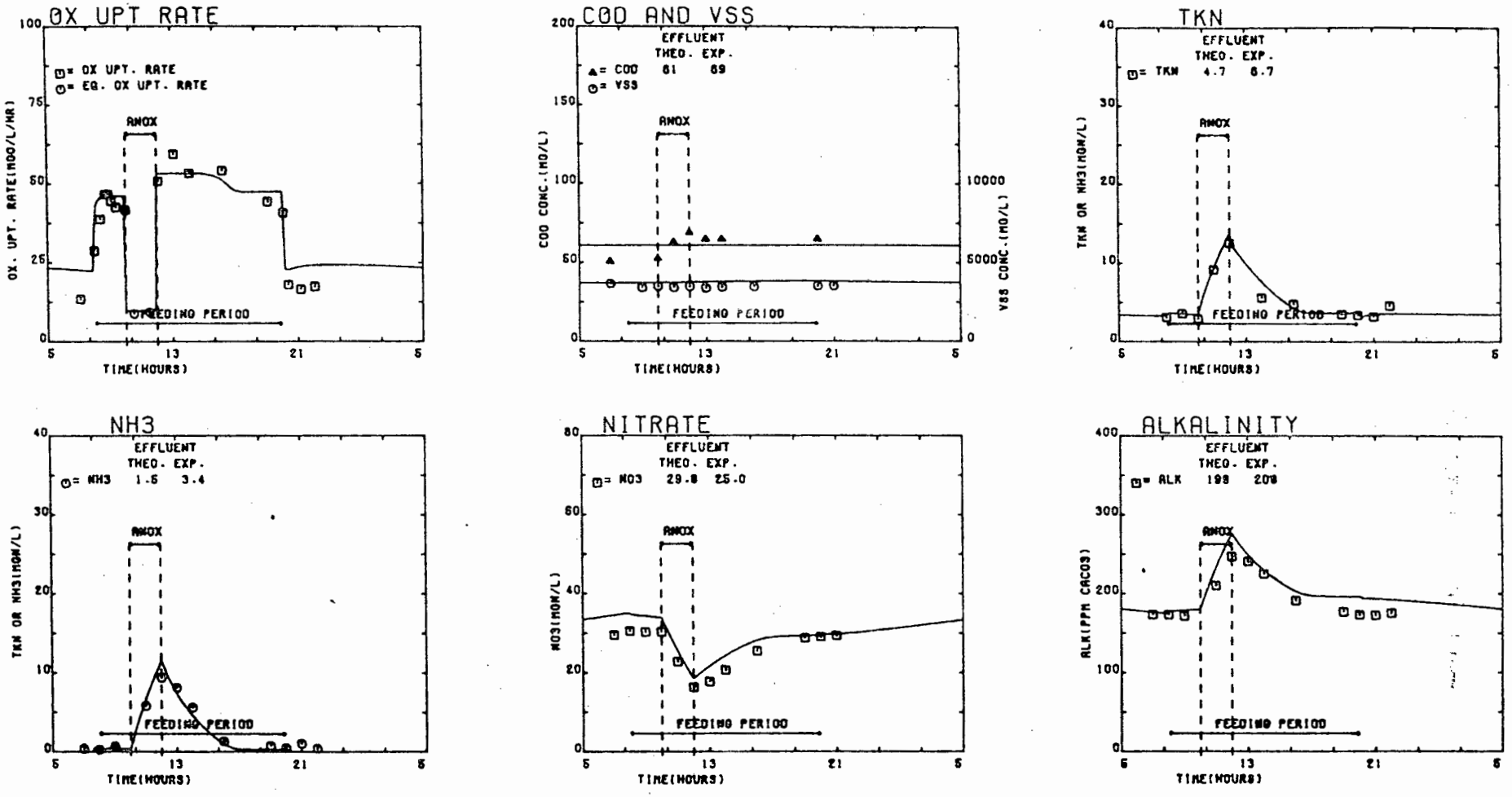

Fig 22 Predicted response using the bisubstrate death-regeneration model compared to observed response in a single reactor CMASP under square wave daily cyclic loading conditions with an unaerated phase during the loading period. Sludge age = 15 days; temp = 14°C; raw sewage as influent (after Sehayek and Marais, 1981).

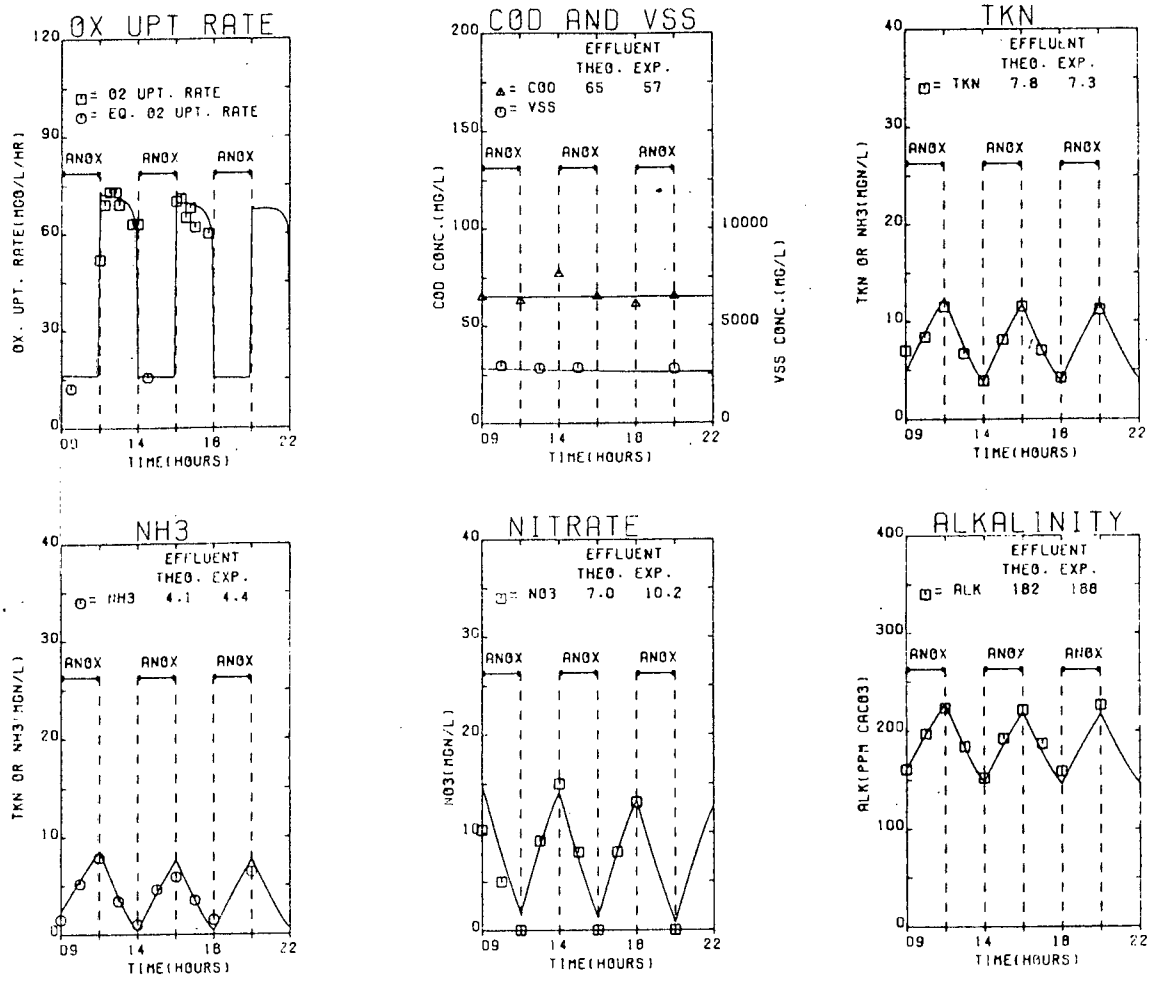

Fig 23 Predicted response using the bisubstrate death-regeneration model compared to observed response in a single reactor CMASP under steady state loading conditions with sequential aerated/unaerated periods each of 2 hours with raw sewage as influent. Influent COD = 496 mgCOD/ℓ; TKN = 47 mgN/ℓ; sludge age = 6 days; temp = 20°C (after van Haandel and Marais, 1981).

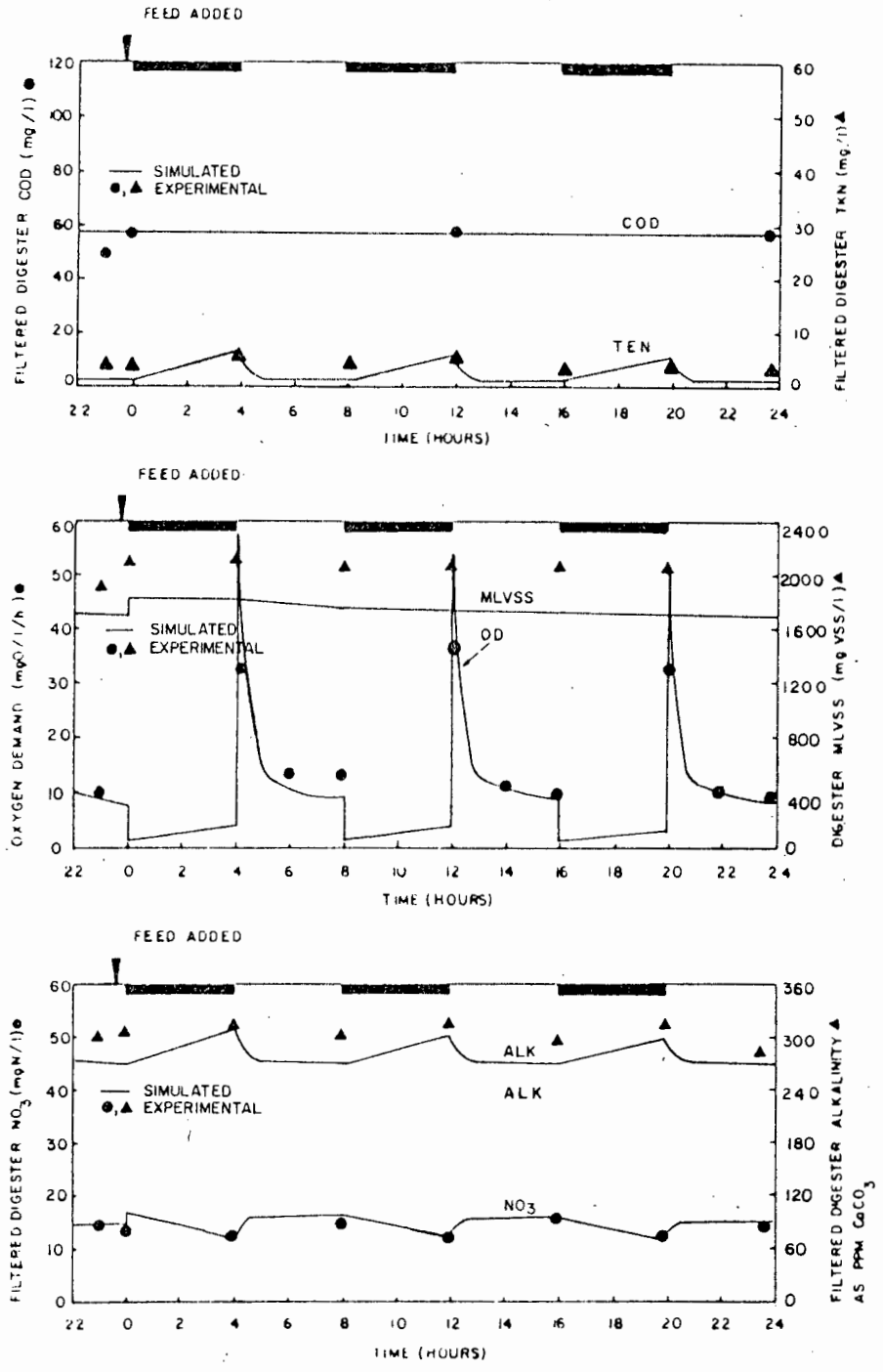

Fig 24 Predicted response using the bisubstrate death-regeneration model compared to observed response in a digester receiving a daily slug of waste activated sludge from a CMASP operated at 4 days sludge age, raw sewage (500 mgCOD/ℓ) as influent. Digester retention time = 6 days; sequential unaerated/aerated periods each of 4 hours; temp = 20°C (after Warner et al., 1983).

dominating influence of the recycling of energy generated within itself.

(4) Due to particulate substrate from death, simulation shows that the ratio (X_s/X_a) never can decrease to zero, but attains a relatively stable state of approximately 0,1 once the sludge age exceeds about 2 days. We noted earlier that the term ($f_{ma} - X_s/X_a$) is a measure of the unoccupied adsorption sites in the Levenspiel surface reaction approach. From simulations with the death-regeneration model of the completely mixed aerobic process treating raw sewage, for sludge ages from 1 to 25 days, at 16°C, the term ($f_{ma} - X_s/X_a$) is plotted versus sludge age in Fig 25. Clearly once the sludge age exceeds about 2 days the fraction of unoccupied adsorption sites becomes substantially constant. When this happens one can expect the organism response to soluble COD effectively will become independent of the particulate COD, justifying the assumption that the different substrate fractions are utilized independently by the same surrogate mass. However, for conditions equivalent to those at sludge ages less than 2 days, this independence no longer seems acceptable; this may provide an explanation for the need to reduce the specific rate of utilization of soluble readily biodegradable COD observed experimentally in the contact reactor of the contact stabilization process as noted earlier. This is an aspect that merits attention as its resolution would provide evidence for or against the death-regeneration approach.

CONCLUSIONS

The following main conclusions can be drawn from this presentation:

1. The level of organization of mixed microbial cultures, from an ecological point of view, is that defined by a community of microorganism populations, with strong population interactions. The ecosystem responds as an entity to input substrate and abiotic factors so much so, that its behaviour can be approximated by a surrogate mass that has behavioural characteristics that give rise to the observed response. Single species cultures, in contrast, have no species

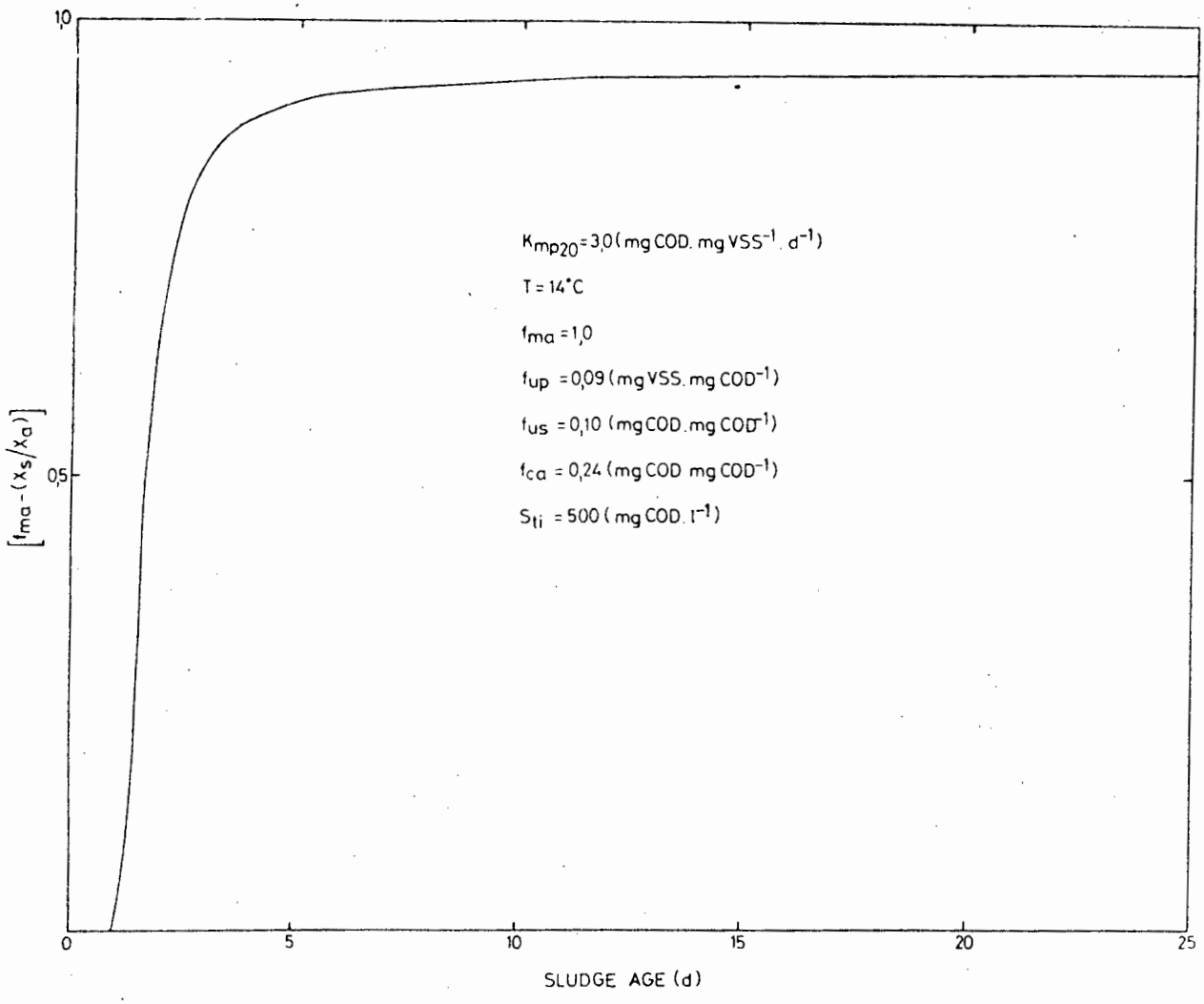

Fig 25 Theoretical plot of fraction unoccupied adsorption sites as a function of sludge age as predicted by the bisubstrate death-regeneration model with raw sewage as influent (after Sehayek and Marais, 1981).

interaction so that, in general, great caution should be exercised in extrapolating single species behavioural patterns to mixed cultures.

2. Endogenous mass loss in mixed cultures appears to be due principally to organism interactions; for example, a prey-predation effect. The material "released" on death provides substrate for synthesis of microbial mass i.e. regeneration of mass. Behaviour under anaerobic/aerobic operation indicates that "death" is continuous and proportional to the live mass. Synthesis takes place only if an electron acceptor (oxygen or nitrate) is available; when absent the dead material accumulates and adds to the substrate mass introduced from outside sources. In terms of this description one can hypothesize a surrogate mass which either exhibits the high "endogenous" mass loss or in which death and regeneration takes place to give an equivalent mass loss.

3. Organic substrate is best characterised by its available electron content, measured equivalently by the mass of oxygen necessary to accept all the available electrons in the organic sample i.e. by means of the Chemical Oxygen Demand (COD) test. Electrons cannot be destroyed; consequently, in steady state operation of a CMASP, for example, the mass input COD per day always must equal the sum of the mass output of COD per day in the effluent and the sludge wastage stream plus the mass of oxygen utilized. This balance constitutes a powerful check in any investigation, dynamic or steady state.

4. The energy per electron available in mixed substrates is very nearly constant so that the transfer of electrons to synthesized material or to oxygen traces the transfer of the energy accordingly. In this manner the energy flow through the system can be traced, by following the destination of the electrons.

5. The input COD from municipal sources can be categorised into four fractions: (i) unbiodegradable soluble; (ii) unbiodegradable

particulate; (iii) readily biodegradable soluble; and (iv) slowly biodegradable particulate. With regard to the utilization of these fractions by the surrogate microbial mass: (i) passes unaffected through the process and is discharged with the effluent; (ii) is enmeshed in the sludge matrix and is discharged via the sludge wastage stream; (iii) is metabolised directly and rapidly, approximately in accordance with Monod's specific growth rate equation; and (iv) is enmeshed in the sludge matrix, adsorbed and stored on the organism where it is broken down by hydrolytic enzymes, whereupon it is absorbed and metabolised as with (iii) above. The governing rate appears to be the hydrolytic action and its rate appears to conform to a surface mediated reaction which can be modelled by a modification of Levenspiel's surface reaction theory. Thus, insofar as the total biodegradable substrate fraction is concerned, it is of a bisubstrate nature in which each fraction reacts very differently from the other.

6. Incorporating the bisubstrate categorization of the influent biodegradable material and the equivalent endogenous mass loss hypothesis of the surrogate mass, the response of aerobic processes, under both steady and dynamic states of operation, can be accurately modelled; however, the model is inadequate to describe process behaviour if anaerobic and anoxic zones are incorporated in the process or the process is operated alternatingly in anoxic or anaerobic/aerobic phases.

7. Incorporation of the bisubstrate categorization of the influent and the death-regeneration hypothesis for the surrogate mass in a model, allows the response of both aerobic and anaerobic/anoxic/aerobic systems to be described accurately.

8. Due to enmeshment and adsorption of particulate biodegradable COD, and the relatively low concentration of readily biodegradable soluble COD in domestic wastewaters, the effluent biodegradable soluble COD is highly insensitive to variations in the influent loading pattern to a process, and always near zero for organism retention times greater

than about 2 days. In contrast, the oxygen utilization rate responds very sensitively to changes in biological activity brought about by changes in input load. This is true particularly at short organism retention times (of about 2.5 days). Consequently, the oxygen utilization rate constitutes a powerful parameter in separating out the different biological reactions and quantifying the associated mass and kinetic constants.

REFERENCES

Adams C E, Eckenfelder W W and R M Stein (1974). Modifications to aerobic digester design. Water Res, 8, 213.

Alexander W V, Ekama G A and G v R Marais (1980). The activated sludge process part 2: application of the general kinetic model to the contact stabilization process. Water Res, 14, 1737.

Arkley M J and G v R Marais (1981). The effect of anoxic zone on sludge production and settleability in the activated sludge process. Res Rept W 38, Dept Civ Eng., Univ of Cape Town.

Bauchop T and S R Elsden (1960). The growth of micro-organisms in relation to their energy supply. J Gen Microbiol, 23, 457.

Bhatla M N and A F Gaudy (1965). Role of protozoa in the diphasic exertion of BOD. J San Eng Div, ASCE, 91, SA3, 63.

Blackwell L G (1971). A theoretical and experimental evaluation of the transient response of the activated sludge process. PhD thesis, Clemson Univ, Clemson, S Carolina.

Daigger G T and C P L Grady (1977). A model for the bio-oxidation process based on product formation concepts. Water Res, 11, 1049.

Daigger G T and C P L Grady (1982). The dynamics of microbial growth on soluble substrates. Water Res, 16, 365.

Deinema M G (1972). Bacterial flocculation and production of poly-β-hydroxybutyrate. Appl Microbiol, 24, 857.

Dold P L, Ekama G A and G v R Marais (1980). A general model for the

activated sludge process. Proc 10th IAWPR Conf, Toronto, Prog Wat Tech, 12, 47.

Doudoroff M and R Y Stannier (1959). Role of poly-β-hydroxybutyric acid in the assimilation of organic carbon by bacteria. Nature, 183, 1440.

Duclaux E (1898). Traite de microbiologie, 1, 208.

Dyson R D (1974). Cell Biology: A Molecular Approach, Allyn & Bacon Inc, Boston.

Ekama G A and G v R Marais(1979). Dynamic behaviour of the activated sludge process. Jour Water Poll Control Fed, 51, 534.

Ekama G A and G v R Marais (1982). Report on apple pulping waste treatability. Dept Civ Eng., Univ of Cape Town.

Grady C P L, Harlow L J and R R Riesing (1972). Effects of growth rate and influent substrate concentration on effluent quality from chemostats containing bacteria in pure and mixed culture. Biotech Bioeng, 14, 391.

Harder W and L Dijkhuizen (1976). Mixed substrate utilization. In P S S Dawson (Ed) Microbial Growth, Dowden, Hutchinson and Ross Inc, Pennsylvania.

Herbert D (1958). Recent progress in microbiology. VII International Congress for Microbiology. Ed. G Tunevall, Almquist and Wiksel, Stockholm, pp 381-396.

Holme T (1957). Continuous culture studies on glycogen synthesis in Escherichia coli B. Acta Chem Scand, 11, 763.

Holme T and H Palmstierna (1956). Changes in glycogen and nitrogen-containing compounds in Escherichia Coli B during growth in deficient media. Acta Chem Scand, 10, 578.

Jacquart J C, Lefort D and J M Rovel (1973). An attempt to take account of biological storage in the mathematical analysis of activated sludge behaviour. In S H Jenkins (Ed.) Advances in Water Pollution Research, Pergamon Press, New York.

Kharasch M S and B Sher (1925). J Phys Chem, 29, 625.

Kharasch M S (1929). Bur Stand US J of Res, 2, 359.

Koch A L and C S Deppe (1971). In vivo assay of protein synthesizing capacity of Escherichia coli from slowly growing chemostat cultures. J Mol Biol, 55, 549.

Lawrence A W and P L McCarty (1970). Unified basis for biological treatment design and operation. J San Eng Div, ASCE, 96, SA3, 757.

Lee S E, Koopman B L, Jenkins D and R F Lewis (1982). The effect of aeration basin configuration on activated sludge bulking at low organic loading. Wat Sci Tech, 14, 407.

Levenspiel O (1972). Chemical Reaction Engineering, 2nd Ed, John Wiley, New York, pp 465-469.

MacKechnie I and E A Dawes (1969). An evaluation of the pathways of metabolism of glucose, gluconate and 2-oxogluconate by Psuedomonas aeruginosa by measurement of molar growth yields. J Gen Microbiol, 55, 341.

Macrae R M and J F Wilkinson (1958). Poly-β-hydroxybutyrate metabolism in washed suspensions of Bacillus cereus and Bacillus megaterium. J Gen Microbiology, 19, 210.

Marais G v R and G A Ekama (1976). The activated sludge process Part 1 - steady state behaviour. Water S A, 2, 4, 163.

Mayberry W R, Prochazka G J and W J Payne (1967). Appl Microbiol, 15, 1332.

Mayberry W R, Prochazka G J and W J Payne (1968). Factors derived from studies of aerobic growth in minimal media. J Bacteriol, 96, 1424.

McCarty P L and C F Brodersen (1962). Theory of extended aeration activated sludge. Jour Water Poll Control Fed, 34, 1095.

McKinney R E (1962). Mathematics of complete mixing activated sludge. J San Eng Div, ASCE, 88, Proc Paper 3133, 87.

McKinney R E and R J Ooten (1969). Concepts of complete mixing activated sludge. Trans 19th Eng Confr, Univ of Kansas, 32.

McLellan J C (1969). Aspects of the response of a mixed microbial culture to variations in loading. PhD Thesis, Rice Univ, Houston, Texas.

McLellan J C and A W Busch (1969). Hydraulic and process aspects of reactor design II: Response to variations. Proc 24th Ind Waste Conf, Purdue Univ Eng Bull, Ext Ser No 135, 493.

Monod J (1949). The growth of bacterial cultures. Pasteur Institute, Paris.

Morris J C and W Stumm (1960). Colloidal aspects of waste treatment. Proc Rudolphs Research Conf, Rutgers Univ, June, 1960.

Novick A and I Szilard (1950). Experiments with the chemostat on the spontaneous mutation of bacteria. Proc Natl Acad Sci US, 36, 708.

Odum E P (1971). Fundamentals of Ecology, 3rd ed, W B Saunders, New York, 384.

Painter H A, Denton R S and C Quarmby (1968). Removal of sugars by activated sludge. Water Res, 2, 427.

Payne W T (1970). Energy yields and growth of heterotrophs. Ann Rev Microbiol, pp 17-51.

Penfold W J and D Norris (1912). The relation of concentration of food supply to the generation of bacteria. J Hyg, 12, 527.

Perret C J (1960). A new kinetic model of a growing bacterial population. J Gen Microbiol, 22, 589.

Pirt S J (1965). The maintenance energy of bacteria in growing cultures. Proc Roy Soc, London Ser B, 163, 224.

Porges N, L Jasewicz and S R Hoover (1956). Principles of biological oxidations. In B J McCabe and W W Eckenfelder Jr (Eds). Biological Treatment of Sewage and Industrial Wastes, Vol 1, Reinhold Publ Co, New York, pp 35-48.

Sehayek E and G v R Marais (1981). Kinetics of biological nitrogen removal in the single sludge activated sludge process. Research Report W 41, Dept of Civil Eng, Univ of Cape Town.

Servizi J A and R H Bogan (1963). Free energy as a parameter in biological treatment. J San Eng Div, ASCE, 63, SA3, 17.

Servizi J A and R H Bogan (1964). Thermodynamic aspects of biological oxidation and synthesis. Jour Water Poll Control Fed, 36, 607.

Siegel B V and C E Clifton (1950). Oxidative asimilation of glucose by Escherichia coli. J Bacteriol, 60, 113.

Slater J H (1981). Mixed cultures and microbial communities. In M E Bushell and J H Slater (Eds). Mixed Culture Fermentations, Academic Press, London, pp 1-24.

Stenstrom M K (1975). A dynamic model and computer compatible control strategies for wastewater treatment plants. PhD thesis, Clemson Univ, Clemson, S Carolina.

Terroine E and R Wurmser (1922). Bull Soc Chim Biol, 4, 519.

Trinci A P J and C F Thurston (1976). Transition to the non-growing stage in eukaryatic micro-organisms. In T R G Gray and J R Postgate (Eds). The Survival of Vegetative Microbes, 26th Symposium of the Society of General Microbiology, Univ of Cambridge, Cambridge Univ Press, Cambridge.

Van Gils H W (1964). Bacteriology of activated sludge. Rep Res Inst Publ Hlth Engng, No 32.

Van Haandel A C and G v R Marais (1981). Nitrification and denitrification in the activated sludge process. Research Report W 39, Dept of Civil Eng, Univ of Cape Town.

Van Haandel A C , Ekama G A and G v R Marais (1981). The activated sludge process Part 3 - single sludge denitrification. Water Res, 15, 1135.

Warner A P C, Ekama G A and G v R Marais (1983). Anoxic-aerobic digestion of waste activated sludge. Research Report W 48, Dept Civ Eng, Univ of Cape Town.

Washington D R and L J Hetling (1965). Volatile sludge accumulation in activated sludge plants. Jour Water Poll Control Fed, 37, 499.

Wooldridge V R and A F S Standfast (1936). Biochem J, 30, 149.

Wright D N and W R Lockhart (1965). Effects of growth rate and limiting substrate on glucose metabolism in Escherichia coli. Jour Bacteriol, 89, 1082.

The Activated Sludge Process Part I – Steady State Behaviour

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Abstract

This paper attempts a general reorganisation of the activated sludge process theory at steady state in terms of the sludge age. Equations are presented for calculating the masses of active, endogenous residue and inert volatile material in the reactor. These are integrated with the oxygen demand. Investigation in nitrification klnetics indicates that in municipal wastewaters the rate limiting step is the conversion of organic TKN to the NH_4^+ form. New methods are presented to determine the yield constant, Y, endogenous respiration constant, b, and the substrate conversion rate constant, K.

A critical analysis is given of existing design criteria in terms of the sludge loading rate and a procedure for design in terms of sludge age is set out.

Introduction

When attempting to trace the development of the theory of activated sludge process over the past 25 years, one encounters an array of papers bewildering in their number and diversity of point of view. Only a thorough study will allow recognition and assessment of original ideas contributed during this period. Whereas most papers contribute in some fashion to the totality of understanding of the process only a few, in the opinion of the authors, are of major significance.

McKinney (1962) made a major contribution by presenting the first rational kinetic theory for the completely mixed activated sludge process (see also McKinney and Ooten, 1969). McKinney established the importance of sludge age (i.e. organism retention time), the food/micro-organism ratio and the division of the sludge mass into active, endogenous residue and inert fractions. He presented formulations for the steady state concentrations in the reactor for the nutrient, the active, endogenous residue and inert volatile fractions and, the oxygen consumption rate. His hypothesis on the rate of nutrient utilization however, differed fundamentally from that proposed by Monod (1950) whose hypothesis found substantial support from many investigators. The two hypotheses have led to controversy that exists to the present day (Goodman and Englande, 1972; Garret, 1972; and Marais, 1973). McKinney's work has had an immense fertilizing effect on the development of the theory of the activated sludge process.

Lawrence and McCarty (1970) presented a unified approach to biodegradation kinetics based on the Monod hypothesis for nutrient utilization. *Inter alia* they considered the activated sludge process where, in particular, they clarified the connection between the food/micro-organism ratio (load factor) and the sludge age. Their presentation is incomplete in that they omitted to incorporate the inert and endogenous mass fractions of the sludge generated in process. This paper is perhaps the most significant subsequent to McKinney's.

A comparison of the Lawrence and McCarty and McKinney theories (Appendix A), shows that for all practical purposes the two theories will produce virtually identical designs if, as is usual in practice, the same load factors (or sludge ages) and sludge concentrations are specified. From a theoretical point of view however, the McKinney approach implies that the effluent quality is a function of the hydraulic retention time and independent of the sludge age, whereas the Lawrence and McCarty approach implies that the effluent quality is a function of the sludge age and independent of the hydraulic retention time. However, the constants assigned in each of the approaches to determine the effluent quality are such that the difference in effluent quality is inconsequential. It is only in this aspect, i.e. in the determination of effluent quality, that the two theories differ. In other respects it can be shown that identical equations apply to determine sludge concentrations and oxygen demand (Marais, 1973).

In this paper Monod's approach is utilized for the reason that in the opinion of the authors the balance of experimental evidence, however inconclusive, favours Monod's hypothesis. But even Monod's approach is deficient and needs augmentation to give predictions in reasonable accord with experimental results when applied to the dynamic behaviour of the activated sludge process. Andrews and Busby (1973) proposed an adsorption and storage mechanism to precede the actual nutrient utilization by the organism. With this mechanism, the nutrient concentration is no longer directly related to the sludge growth rate, as required by the Monod hypothesis, but only applies in the special case when steady state conditions are operative. The hypothesis of Andrews, duly modified, has proved of crucial importance to the work reported in this series of papers.

The work of Eckenfelder (1967) and his group was outstanding in converting the theoretical concepts into practical design procedures. Their procedures were based on *ad hoc* experimental investigations into each waste, to obtain design parameters. As a theoretical framework for the experimental procedures they utilized a simplified Monod approach. At the time no practical method existed to separate out experimentally the active and non-active fractions of the sludge and accordingly the volatile solids were accepted as representative of the active frac-

tion. By making this approximation the approach became semi-empirical which, though eminently practical and useful, did not contribute to the theoretical development of the kinetic theory. Eckenfelder, probably more so than any other engineer, was instrumental in establishing new design procedures for the activated sludge process.

There are two papers, not directly concerned with degradation kinetics, which are of major significance in providing a basis for the rational development of the kinetic theory. Eckenfelder and Weston (1956) established that there is an approximate proportionality between the mass of volatile solids and the Chemical Oxygen Demand (COD) of the mass, as follows; $\Delta COD = 1{,}42\ \Delta VSS$. Servizi and Bogan (1963) established that when an organic material is oxidized the energy released is proportional to the oxygen consumed. As the COD is a measure of the oxygen necessary to oxidize the volatile material, then from Servizi and Bogan's work the COD is a measure (in terms of oxygen equivalent) of the energy in the volatile solids. Hence it is possible to express the energy in the wastewater and at any point in the process either in terms of equivalent oxygen or equivalent volatile solids. These two papers established the importance of the COD test as a basic measure of energy and marks the beginning of the decline of the BOD test.

The survey above dealt principally with carbonaceous energy removal kinetics. Downing, Painter and Knowles (1964) clarified the nitrification behaviour of the activated sludge process. In this endeavour their successful employment of Monod's hypothesis did much to establish the value of this approach in the wider field of biological degradation kinetics. The work of Downing *et al* established the minimum sludge age necessary for nitrification at a particular temperature. In this respect the theory appears to be adequate. However, application to laboratory scale plants operating under cyclic flow conditions treating settled sewage show that a factor limiting the rate of nitrification is the necessary conversion of TKN to saline ammonia before nitrification can take place, i.e. the rôle of nitrification is limited to a degree by the rate of production of saline ammonia. This aspect is treated in depth in this series of papers.

In the practical application of the activated sludge process it is evident that American practice initially was concerned principally with the removal of carbonaceous energy. This was adequately accomplished by having short sludge ages, or equivalently, high load factors. Nitrification tended to be regarded as undesirable and, on occasion, the literature records procedures on how to suppress nitrification, for example, by reducing the MLVSS, i.e. reducing the sludge age, or equivalently, increasing the load factor. The problems associated with nitrifying plants are consequently not well documented.

Application of the activated sludge process in tropical and semi-tropical countries exposed new problems. Where the water temperatures range 22°C upwards it is virtually impossible to design a process in which nitrification will not occur; nitrification takes place at sludge ages of 2,5 days or less. In those regions nitrification must be accepted as inevitable. Furthermore, to reduce the deleterious effect of ammonia discharge on aquatic life, in some countries nitrified effluents have become obligatory. In temperate climates this demands long sludge ages or special nitrification processes, for example the three sludge process (Barth, Brenner and Lewis, 1968).

Incorporation of nitrification in the normal activated sludge process requires changes in design and operating procedures. An illustrative example is the function of the secondary settling tank. In plants with no nitrification the settling tank serves two functions, solids-liquid separation and sludge thickening. To obtain high underflow concentrations the recycle ratio is kept low; 0,25 to 1,0. Accumulation of sludge mass in the settling tank is large and the sludge is retained for an appreciable length of time in the settling tank. In plants with nitrification sludge retention in the settling tank causes denitrification, consequent flotation of sludge particles and sludge loss over the effluent weirs. To counter these effects the practice has developed of using high recycle ratios of 1:1 to 2,5:1. This reduces the retention time of the sludge in the settling tank but concomitantly reduces the concentration of sludge in the underflow so that wasted sludge from the underflow no longer can be discharged directly to the anaerobic digestors. In effect, the function of the secondary tank is reduced to that of clarification only.

In the cold and warm temperate climates when nitrification is essential, the sludge age is necessarily doubled and trebled over that required for carbonaceous energy removal only. The effluent quality is no longer a factor in design as there is little change in the unmetabolized BOD in the effluent for sludge ages greater than about 4 days. The causes leading to poor liquid-solids separation at short sludge ages are also absent, although poor settling due to other causes may now appear at long sludge ages. The composition of the sludge changes, the inert fraction becomes significant at long sludge ages whereas it is negligible at short ages. The total mass of sludge to be retained in the plant is doubled or trebled; this in turn requires that the hydraulic retention time (or reactor volume) be increased substantially otherwise the concentration of sludge is so great that difficulties are experienced in supplying adequate oxygen and mixing and obtaining satisfactory liquid-solids separation.

Although the effects of these factors change gradually with increasing sludge age, nitrification requirements have resulted in a sudden 'jump' in the sludge age beyond the value for which a background of experience is available. Some of the theory and empirical rules previously satisfactory, now prove inadequate or deficient. This applies particularly to the calculation of the sludge mass and oxygen requirements. In fact, the established design procedure becomes uncertain and plants may be over- or under-designed.

Besides the uncertainty in design procedure and process response discussed above, other developments have led to further complicating factors in design.

Barnard (1973; 1975) developed a practical biological denitrification process configuration for the activated sludge process using influent wastewater as the source of energy for denitrification. He subsequently reported that this configuration also induces enhanced phosphorus removal. These developments have opened up new avenues of research and application. There is little doubt that the activated sludge process, configurations and operation of the future will differ substantially from those of the past.

Six years ago a program of research into the activated sludge process was initiated at the University of Cape Town. Research aspects included the kinetics of synthesis, endogenous respira-

tion, oxygen utlization, sludge accumulation, nitrification and aerobic digestion under steady and dynamic state operating conditions. Investigations into biological denitrification and phosphorus removal were initiated when these processes were shown to have practical possibilities. From the commencement of the investigations only settled and unsettled sewage were used as influents to the test units so that the derived parameters could be directly useful for design. Throughout the carbonaceous waste strength was measured by means of the Chemical Oxygen Demand test.

The outcome of this research is now presented in a series of four papers on the activated sludge process, dealing in turn with (1) Steady state behaviour, (2) Dynamic state behaviour, (3) Biological phosphorus removal and (4) Biological denitrification using wastewater as electron donor.

Objectives of Wastewater Treatment

Life requires a continuous throughput of (1) mass and (2) energy for synthesis and cell maintenance. (1) The principal mass elements passing through the life system are Hydrogen, Oxygen, Carbon, Nitrogen and Phosphorus. (2) Energy is principally derived from three sources and these form a convenient criterion to categorise the organisms implicated:

(a) Radiation – photo synthetic autotrophs
(b) Organic compounds – heterotrophs
(c) Inorganic compounds – chemical autotrophs

In the biosphere the fundamental source of energy is solar radiation. The photo-synthetic autotrophic cells fix a small fraction of the solar energy by forming a complex high energy organic compound – glucose. Of the mass requirements the elements H and O are obtained from H_2O; Carbon (C) from CO_2; Both H_2O and CO_2 are readily available whereas the availability of Phosphorus (P) and Nitrogen (N) is usually limited. Phosphorus does not readily occur in soluble form and nitrogen is useful to the organism only in the NH_4^- and NO_3^- forms. The restricted availability of these two elements usually forms the limitation on the mass of autotrophic life, a body of water for example, can sustain. For this reason Phosphorus and Nitrogen are termed eutrophic (life giving) substances. Whereas Phosphorus is limited by the mass available or entering a particular ecosystem, ammonia can be generated from dissolved molecular nitrogen by certain micro-organisms. In this respect the control of Phosphorus in a body of water takes on a greater significance than the control of Nitrogen.

The glucose synthesized by the autotrophs forms the basic source of energy for the heterotrophic cells to synthesize the more complex molecules that constitute the cell mass, including proteins. Again only a fraction of the energy utilized is converted into cell mass, the balance is lost as heat. In this fashion through the sequential chain of life there is a continuous reduction of the total organic energy originally fixed by the photosynthetic autotrophs. When the organic energy reduces to zero heterotrophic life ceases.

In wastewater microbiology the chemical autotrophs occupy a position of special importance. They derive energy from saline ammonia and nitrites, to form nitrates. As shown earlier, nitrates and saline ammonia are eutrophic substances.

From these considerations the objectives of wastewater treatment are seen to be twofold:

(1) Reduction of organic bound energy to a level where it can no longer sustain heterotrophic growth, and
(2) Reduction of the eutrophic substances, phosphates, ammonia and nitrates, to levels where the photosynthetic autotrophic micro-organisms are limited in their growth, and therefore their capacity to fix solar energy as organic energy in the body of receiving water is reduced.

Oxygen Demand Tests

The process of heterotrophic energy abstraction from a complex carbonaceous molecule consists of splitting the molecule, which releases CO_2, H^+ and energy. The CO_2 escapes as gas but the hydrogen ion remains and must be removed for the process to continue. This is achieved by attaching it to hydrogen ion acceptor. In aerobic conditions the hydrogen ion acceptor is oxygen, to yield water. From the work of Servizi and Bogan (1963) the energy released is proportional to the oxygen utilized. In this fashion the potential oxygen demand is a measure of the energy which can be released for metabolism. By using the oxygen as a measuring stick one may, in this indirect fashion, measure the progress of carbonaceous energy release in the biological system.

The energy release or equivalent oxygen demand for the chemical autotrophs or nitrifying organisms form a separate system from that of the heterotrophs. Oxygen is utilized to convert NH_3^- to NO_2^- to NO_3^-. The saline and bound ammonia is measured directly by the Total Kjeldahl Nitrogen (TKN) test. It is not necessary to measure experimentally the oxygen demand to convert the ammonia to, say, nitrate as the ammonia has a known chemical composition so that once its mass is known the mass of oxygen necessary for conversion can be calculated. This procedure would also be valid for a carbonaceous material if the chemical structure is known, but this unfortunately, is not possible for the infinity of organic products in wastewaters.

There are two tests currently employed to measure the carbonaceous energy content of the waste via its oxygen demand, the Biochemical Oxygen Demand (BOD) and the Chemical Oxygen Demand (COD) tests. Ideally these two tests should measure only the energy released in the breakdown of carbonaceous compounds and proteins to the ammonia stage.

The BOD test is an empirical one performed under strictly specified conditions and procedures; any deviation may give rise to very uncertain results. In the 5-day BOD (BOD_5) test the sample of wastewater is suitably diluted with well-oxygenated water and micro-organisms adapted to the waste introduced, if necessary. The oxygen concentration is determined and the sample stored in darkness at 20°C for 5 days. The difference in oxygen concentration between the beginning and end of the test period gives the 5-day BOD value. In the Ultimate Oxygen Demand (UOD) test, the sample is stored for about 20 days at 20°C to provide sufficient time for total utilization of the biodegradable carbonaceous energy.

In the BOD_5 test biological activity is still continuing at the end of 5 days. In the UOD test, biological activity has virtually ceased at the end of 20 days, but a fraction of the energy origi-

TABLE 1

EXPERIMENTAL COD/VSS RATIOS

Sludge	COD/VSS ratio	96% Conf. interval	No. of tests
Activated sludge (Bellville plant)	1,43	± 0,01	230
Lab. CMAS Units R_s 3 to 30 days	1,48	± 0,08	120
Aerobic digested sludge from lab. CMAS units	1,45	± 0,17	80
Raw sewage (Athlone)	1,45	± 0,04	180
Wine distillery raw waste	1,43	± 0,10	13

nally in the waste remains as unbiodegradable endogenous residue of the bacteria synthesized from the waste. Both tests therefore underestimate the energy (in terms of oxygen) in the water in varying proportions. The 20 day test probably gives the most stable relative measure of the biodegradable carbonaceous energy, but the time element makes the test impractical for routine use. If the UOD/BOD_5 ratio remains constant, the 5 day value would serve as a satisfactory relative measure. However, the ratio varies for the different types of raw wastes, and for a particular waste, it varies from one point in the bioprocess to another.

Low BOD values are obtained if the organisms are not adapted to the waste; some heavy metals kill organisms or inhibit their action; nitrifying organisms in the test sample may multiply and utilize oxygen to convert NH_3 to NO_3, to give an inflated value for the carbonaceous energy, unless nitrification is deliberately suppressed by chemical additives.

The COD test gives a measure of the total energy in terms of oxygen by oxidizing the organic waste with an oxidizing agent, potassium dichromate. Ammonia is not oxidized so that the test value reflects only the energy release due to oxidation of the carbonaceous compounds. The test takes two hours. Some organic compounds derived from industrial sources such as the aromatic hydrocarbons and pyridenes are not broken down in the test but are utilized by the micro-organisms. In such instances, the COD test is not so reliable. However, normally a very high percentage, about 95 per cent, of the carbonaceous compounds are oxidized.

In terms of the time the organic material is under attack in a treatment plant, a fraction of the waste is unbiodegradable, i.e. the energy is unavailable for biological metabolism. The COD test, however, oxidizes both the biologically degradable and the unbiodegradable materials, hence usually the test overestimates the energy available for biological action. However, this does not reduce the utility of the test. If one makes the reasonable assumption that the small fraction of organic material in the wastewater *not* oxidized in the COD test, remains constant, then any change in COD between two points in the process provides an assessment (in terms of oxygen) of the corresponding energy change.

The change in COD, ΔCOD, is utilized to establish the kinetics of energy conversion in the process, i.e. the energy removal can be directly linked to the COD change without any correction constants. In contrast, using ΔBOD_5 values requires a correction factor as the test values do not reflect the total oxygen demand. Consequently the change in BOD_5 underestimates the energy change.

A great advantage of the COD test is that it provides a direct estimate of the oxygen or energy potential of the volatile solids. It was stated earlier that the major fraction of energy required for metabolism is obtained by splitting the hydrogen bonds in the organic molecule and attaching the hydrogen ion to a hydrogen ion acceptor, usually oxygen. Based on the average stoichiometric composition of microbial sludge, ($C_5H_2NO_2$), Eckenfelder and Weston (1956) calculated the theoretical mass of oxygen necessary to oxidize the mass of hydrogen ions per unit of organic mass as:

$$1 \text{ mg VSS} \rightarrow 1{,}42 \text{ mg } O_2 \rightarrow 1{,}42 \text{ mg COD} \qquad (1)$$

i.e.

$$\frac{\text{COD}}{\text{VSS}} = 1{,}42 \qquad (2)$$

This theoretical ratio can be expected to be only approximately correct, as the ratio of hydrogen mass to total molecular mass will depend on the structure of the organic material. In particular, the influent VSS is likely to give rise to a COD/VSS ratio different from that for bacterial mass as the volatile solids are derived from many sources. Experimental data by Eckenfelder and Weston supported their derived theoretical value but the data were obtained only on bacterial mass developed from a soluble waste. No comprehensive investigations have been reported to establish the validity of this ratio for the volatile solids from normal activated sludge treating municipal wastes. To correct this deficiency, an extensive series of tests on raw sewage, activated sludge MLVSS and aerobic digested activated sludge were undertaken. The mean values obtained for the COD/VSS ratios are listed in Table 1. Figure 1 shows the COD/VSS ratios obtained from a series of tests on completely mixed laboratory scale activated sludge units over a range of sludge ages from 2,5 to 30 days. Evidently the ratio remains approximately constant, independent of the sludge age. Taking all the data into account, the ratio COD/VSS is very near the theoretical value of 1,42 – perhaps slightly higher, 1,46. In the absence of more conclusive data, the value of 1,42 for the ratio has been accepted in this paper (Marsden and Goloi, 1973).

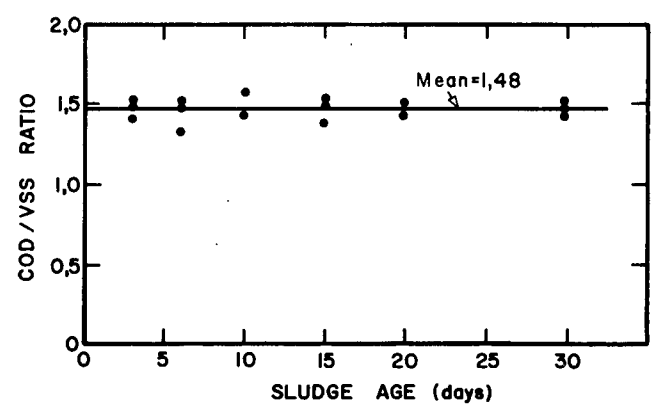

Figure 1
Relationship of COD/VSS ratio with sludge age in a completely mixed activated sludge plant

TABLE 2

COD/BOD RATIO (SETTLED SEWAGE)

	Mean	Range	No. of data
Smith and Eilers (1969)	2,06	1,90–2,27	12
Boon and Burgess (1972)	1,88	1,73–2,23	17
Dixon *et al* (1972)	2,04*	1,95–2,16	–

*Average of four years operation, 1967–1970

The equivalence of VSS and COD (Eq. 2) is of the greatest utility when investigating the kinetics of the activated sludge process. It allows a balance to be made between the daily energy entering the plant and that leaving via the sludge wasted, the effluent and as heat, the last named being the daily oxygen mass required.

From data abstracted from the literature and listed in Table 2, there appears to be an approximate relationship between COD and BOD_5, for *municipal settled sewage*, i.e.

$$COD = 2\ BOD_5 \quad (3)$$

Approximately 5 to 10 per cent of the influent COD is unbiodegradable, i.e.

$$COD\ (bio) = (1{,}8\ to\ 1{,}9)\ BOD_5 \quad (4)$$

The COD/BOD_5 ratio changes as the waste passes through the plant, usually increasing. The reason for this is that the unbiodegradable fraction in the influent remains relatively unaffected in its passage through the plant, whereas the biodegradable fraction decreases.

Should it be decided to change the energy parameter from BOD_5 to COD, the approximate relationship between COD and BOD_5 for settled sewage influent is particularly useful during the transition period. The kinetic equations developed in terms of COD can be directly modified and written in terms of BOD_5 (see later).

Considering the effluent discharged from a plant, the BOD_5 value gives a relative but uncertain measure of the energy still available for rapid biological action in the receiving stream. Unless the appropriate ratio UOD/BOD_5 for the effluent is available, the 5-day test value can be only a rough indication of the pollution potential of the discharge. The BOD_5 test also gives no assessment of the unbiodegradable fraction in the effluent. The COD test gives an assessment of the sum of the biodegradable and unbiodegradable fractions in the effluent but these two cannot be separated directly in the test. However, if the plant's kinetic behaviour is taken into account, it is possible to estimate the unbiodegradable and biodegradable fractions in the effluent and influent.

There is an enormous 'prejudice of previous experience' in favour of the BOD_5 test. The standardization of the COD test, the short time necessary for the test, the relative ease with which it can be automated and its direct link with the energy in the water provide a powerful incentive to replace the BOD_5 by the COD test in wastewater treatment technology.

Biological Growth Kinetics

When an organism is brought into contact with a biodegradable energy (nutrient or substrate) source, the response can be described by the following conceptual model:

(1) The COD is removed from the liquid on to the organism mass, that is, storage of energy on the organism takes place.

(2) The stored energy is utilized by the organism to synthesize organism mass: a fraction of the energy is incorporated as organism mass, the rest is lost as heat. The fraction lost as heat is directly proportional to the oxygen utilized. The synthesis process is called anabolism.

(3) Concomitantly with (2) above, but distinct from it, there is a loss of live mass to provide energy for cell maintenance, called endogenous respiration. Not all the live mass that disappears *per se* is lost as energy, a fraction remains (approximately 20 per cent) as unbiodegradable organic residue, called endogenous residue. A mass of oxygen must be supplied proportionately to the *volatile mass* that disappears from the *system*. This process is called catabolism.

Processes (1), (2) and (3) constitute the metabolism of the organism. Such a simplistic model obviously cannot describe completely the complex organism metabolism. Its merit is that under certain conditions it gives an adequate description of the observed behaviour in terms of the energy and volatile mass parameters. The separation and simultaneous occurrence of synthesis and endogenous mass loss may be particularly difficult to visualize but the separation of these two phenomena is perhaps better appreciated by applying the model to the human organism.

Quantitization of the model requires answers to the following questions:

1. At what rate is the energy removed from the liquid?
2. What fraction of the input energy is incorporated as cell mass?
3. At what rate is the energy incorporated into the cell?
4. What is the rate of endogenous mass loss?

COD removal and COD utilization and yield

From an extensive series of experiments Porges, Jasewics and Hoover (1956) concluded that an appreciable mass of nutrient (COD) can be stored on the organism and that the rate of storage can exceed the rate of COD utilization by a factor of up to 2,6 times. They estimated storage potential up to 50 per cent of the mass of organisms measured as COD.

Monod derived an empirical relationship, relating the concentration of nutrient surrounding the organisms with the rate of mass growth of the organism (Eq. 8). Gaudy, Obayashi and Gaudy (1971) provided experimental evidence that Monod's relationship does not appear to be valid for a period after a step change in nutrient concentration. The organisms did not re-

spond immediately to the change in nutrient concentration as expected from Monod's equation: after a step increase the organisms continued, for period, to remove nutrient at the old rate then gradually the rate increased to a new steady state level. They ascribed this behaviour to a need for the organism to develop additional nutrient adsorption sites and concluded that Monod's rate function is valid only under steady state conditions. (From their description of Monod's experimental procedure it would appear that his results were obtained from near steady state conditions).

At the University of Cape Town an experimental study was undertaken to measure the response of laboratory scale completely mixed activated plants under daily cyclic square wave of wastewater addition and flow. After the commencement of the feed period, the COD rapidly disappeared from the liquid but the oxygen utilization rate was significantly less than that expected from the observed removal rate of COD if synthesis was taking place directly. Some storage of the nutrient was taking place. When the feed terminated the carbonaceous oxygen utilization rate continued for some time at the same rate as during feed, then gradually decreased, until fairly abruptly the rate steadied at that associated with endogenous respiration. The behaviour subsequent to feed termination indicated that stored nutrient was available to sustain the high rate of synthesis oxygen demand. It further indicated that the rate of utilization of the stored material was a function of the concentration of stored material remaining – as the stored material was depleted a concomitant reduction took place in oxygen utilization rate. True endogenous respiration was only evident after the stored material was completely metabolized.

It is not clear in what fashion the behaviour observed by Gaudy *et al* fits the behavioural pattern observed under daily cyclic flow. The conditions under which the two investigations were done were very different; in the cyclic flow investigation, the organism concentration was so high that the nutrient added was removed virtually within minutes, whereas Gaudy *et al* utilized a small mass of organisms in a large mass of nutrient, so large that the nutrient concentration remained substantially constant during a test. As Gaudy *et al* did not measure the oxygen utilization rate, it is not possible to determine from their work whether the storage effect was present. The mechanism they propose is probably present in transient flow conditions in the activated sludge plant.

Under steady state conditions, Monod's function is not invalidated by the various phenomena described above. The COD utilization rate constant is generally smaller than the storage rate constant, so that with a constant COD concentration surrounding the organism the level of COD storage builds up until the rate of COD going into storage is equal to the rate of utilization of stored COD. Thus, at steady state, the storage phenomena are effectively by-passed and Monod's relationship apparently applies.

The equations derived below give a quantitative description of the basic phenomena in biological reactions. They are all based on experimental observation and their validity is in a sense only verified for the experimental set-up employed to determine them. In particular Monod's relationship is strictly valid only if the value of the surrounding nutrient concentration, S, remains constant. In transients of S, Eqs. (6 and 7) will not be valid. In the following paper (Ekama and Marais, 1975), which deals with transient phenomena, it will be shown in what respect Eqs. (6 and 7) are incomplete.

For a particular organism population and energy source the fraction of energy synthesized into new cell material appears to be constant with respect to the energy utilized. The fraction of energy converted to cell material (the growth yield coefficient) can be expressed in two ways: in terms of volatile mass (VSS), or in terms of energy (COD). As these two parameters are related by Eq. (2), it is immaterial which one is used, provided the units are consistent. In activated sludge theory it is usually convenient to express the growth yield coefficient in terms of volatile mass:

Let X_a = concentration of organisms (biological or active sludge), (mg VASS/ℓ)

S = concentration of biodegradable energy surrounding the organism (substrate or nutrient) (mg COD/ℓ)

Y = growth yield coefficient, being the mass of organisms synthesized per unit mass of substrate utilized, (mg VASS/mg COD utilized).

The mass synthesized dX_{a1}, with respect to the mass of energy utilized, dS, is given by

$$dX_{a1} = Y\ dS \tag{5}$$

The subscript, 1, designates the active mass synthesized. Writing Eq. (5) in terms of oxygen equivalents, i.e. expressing the volatile mass synthesized as COD, then

$$dCOD_{xa} = dS' = 1{,}42\ Y\ dS \tag{6}$$

The energy lost, or oxygen equivalent lost during synthesis expressed as COD, (dS″), is equal to the oxygen required, dO and is given by the difference between the energy input, dS, and the energy actually synthesized into VSS, dS′, i.e.

$$\begin{aligned} dO = dS'' &= dS - dS' \\ &= dS - 1{,}42Y\ dS \\ &= (1 - 1{,}42Y)dS \end{aligned} \tag{7}$$

A graphical representation of the synthesis reaction for a value of Y = 0,43 is given in Fig. 2. From Fig. 2 if 1 mg of COD is utilized, 0,43 mg of VSS will be synthesized (Eq. 5), which is equivalent to incorporating 1,42 × 0,43 = 0,61 mg COD as synthesized mass (Eq. 6). The oxygen requirement for this synthesis will be 1,0 – 0,61 = 0,39 mg, (Eq. 7).

Monod, working with pure cultures, determined the rate of growth of the organism mass under conditions in which the surrounding nutrient concentration, S, remained relatively constant in a particular experiment, and for a number of such experiments, related the growth rate, μ, to the nutrient concentration, S. He established the following empirical relationship:

$$dX_{a1}/dt = \mu X_a \tag{8}$$

where

$$\mu = \mu_m S/(K_s + S) \tag{9}$$

μ = Specific growth rate at concentration S

μ_m = maximum specific growth rate for the specific organism, substrate and culture conditions (mg VSS/mg VSS/d)

K_s = substrate concentration at which $\mu = 0{,}5\mu_m$ (mg COD/ℓ)

Substituting for dX_{a1} from Eq. (5), then Eq. (8) can be written relating dS/dt to the growth rate – to derive a form widely used in activated sludge treatment kinetics (Eq. 12):

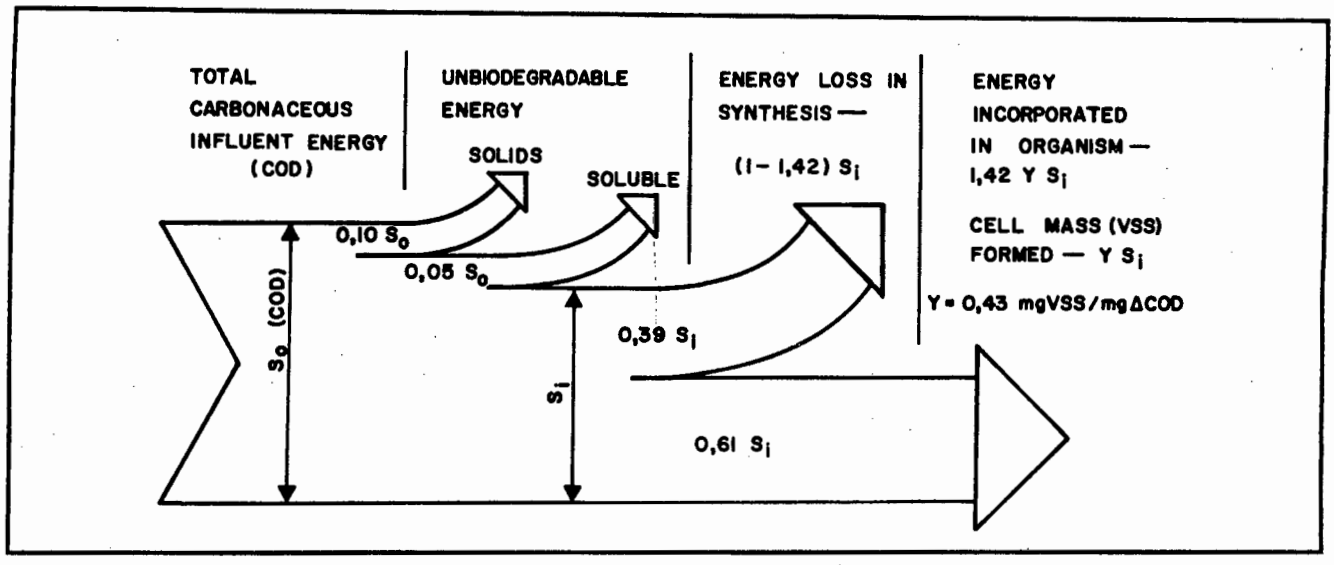

Figure 2

Fractional division of energy (as oxygen equivalent) of influent raw sewage in synthesis process

$$\frac{dX_{a1}}{dt} = Y\frac{dS}{dt} = \frac{\mu_m S}{K_s + S} X_a, \quad (10)$$

i.e.

$$\frac{dS}{dt} = \frac{\mu_m}{Y}\frac{S}{K_s + S} X_a \quad (11)$$

Defining $\frac{\mu_m}{Y} = K_m$,

$$\frac{dS}{dt} = \frac{K_m S}{K_s + S} X_a \quad (12)$$

Conversely, one can now express Eq. (8) in terms of K_m. Substituting Eq. (5) in Eq. (12):

$$\frac{dX_{a1}}{dt} = Y\frac{K_m S}{K_s + S} X_a \quad (13)$$

Equations (12 and 13) are alternative forms of Eqs. (10 and 11) respectively.

Two extreme cases can be defined in Eqs. (12 and 13):

(i) When S is large with respect to K_s then K_s can be neglected and Eq. (13), for example, reduces to

$$\frac{dX_{a1}}{dt} = YK''X_a \quad (14)$$

The conditions under which Eq. (14) applies, have little relevance in the activated sludge process, where the objective is to reduce the substrate concentration surrounding the organism, S, to as low a value as possible.

(ii) When S is small with respect to K_s, then S can be neglected below the line in Eq. (13). Defining $K_m/K_s = K$, then Eq. (12) reduces to

$$\frac{dS}{dt} = KSX_a \quad (15)$$

where K has units ℓ/mg VSS/d, and Eq. (13) to

$$\frac{dX_{a1}}{dt} = YKSX_a \quad (16)$$

Eqs. (15 and 16) find important application in activated sludge kinetics.

Endogenous respiration

Per unit of time, the *nett* mass loss due to endogenous respiration is proportional to the biological active mass, hence the rate of change of live mass due to endogenous respiration can be written

$$\frac{dX_{a2}}{dt} = -bX_a \quad (17)$$

where

b = specific endogenous respiration rate, (mg VASS/mg VASS/d), and the subscript, 2, designates the live mass lost in endogenous respiration.

Only about 80 per cent of the live mass *per se* that disappears is utilized as energy, 20 per cent remains as unbiodegradable endogenous residue, X_e. Let f = the fraction remaining as endogenous residue, then complementary to Eq. (17):

$$\frac{dX_e}{dt} = -\frac{dX_{a2}}{dt}f = fbX_a \quad (18)$$

Hence the mass that physically disappears from the system is given by $(1 - f)bX_a$.

Nett energy released as COD (or oxygen requirements) during endogenous mass loss is given by the oxygen equivalent of the mass that disappears from the system, i.e.

$$\frac{dO}{dt} = 1{,}42\,(1 - f)bX_a \quad (20)$$

A criticism of the concept of endogenous mass loss is that it describes nett behaviour. As a steady state concept this is

adequate, but it may not be so if transient loading conditions are encountered. A more elaborate conceptual model will be presented in the following paper (Ekama and Marais, 1975) where an "actual" endogenous rate will be derived.

Process Kinetics

The section above dealt with the kinetics of biological growth. As such, the equations are general within the limitations mentioned. In the activated sludge process, the mixing régime in the reactor and the sludge return influence the behaviour and response of the process – consideration must be given to reactor kinetics.

There are two extremes of mixing: completely mixed and plug flow.

In the completely mixed régime the influent is instantaneously and thoroughly mixed with the reactor contents. Hence the effluent flow from the reactor has the same constitution as the reactor contents. The reactor effluent flow passes to a settling tank; the overflow from the tank is the stabilized waste stream, the underflow is concentrated mixed liquor and recycled back to the reactor. In the completely mixed system the rate of return of the underflow has no effect on the reactor process except if an undue sludge build-up occurs in the settling tank. The shape of the reactor is approximately square or circular in plan, and mixing is usually by mechanical aerators. Examples are extended aeration plants, aerated lagoons, Dutch ditch and completely mixed activated sludge plants.

In a plug flow régime, the reactor is usually a long channel type basin. The influent is introduced at one end of the channel, flows along the channel axis and is mixed by air sparges set along one side of the channel. Each volume element of liquid along the axis is presumed to remain unmixed with the elements leading and following. Discharge to the settling tank takes place at the other end of the channel. To inoculate the influent waste flow with organisms the underflow from the settling tank is returned to the influent end of the channel. This creates an intermediate flow régime, deviation from true plug flow conditions depending on the magnitude of the recycled underflow. Conventional activated sludge plants are of the intermediate flow régime type with recycle ratio varying from 0,25 to 3 times the influent flow rate. If the recycle rate is raised very high, the mixing régime approaches a completely mixed condition.

Intermediate flow régimes are also achieved by having reactors in series (as in the Huisman Orbol plant), or by step-aeration. In the latter, the influent is fed at a series of points along the axis of the plug flow type reactor. Both configurations require, for inoculation purposes, recycling of the sludge from the settler to the influent point.

When modelling the activated sludge process, simulation of an intermediate mixing régime is always possible by replacing the real system by a series of two or more completely mixed reactors with the appropriate inter reactor flows and feeds. An understanding of the kinetic behaviour of the completely mixed system therefore, is basic to modelling the process over a range of mixing régimes from plug flow to completely mixed.

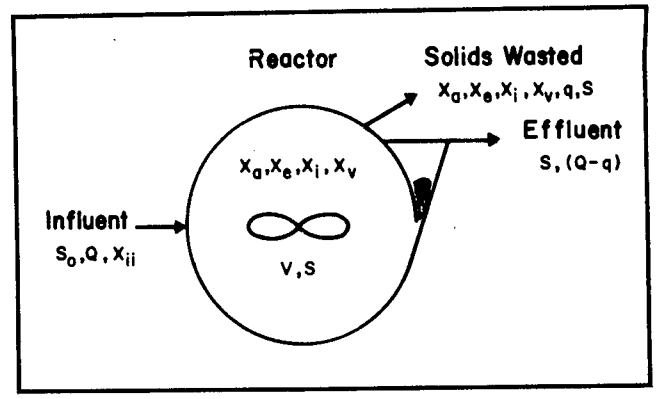

Figure 3
Diagrammatic sketch of completely mixed activated sludge process with sludge wasting from the reactor

Completely mixed activated sludge process kinetics

In the analysis below, although the equations are derived in a form which apparently allows solution of transient conditions, the equations are, in fact, deficient for this purpose as storage effects are ignored. In the following paper (Ekama and Marais, 1975) a more general model will be presented that permits solution under cyclic varying flows and COD concentrations.

In deriving the steady state solutions for the completely mixed activated sludge system, the development follows that of Lawrence and McCarthy (1970). The COD utilization rate relationship is that of Monod simplified to apply at relatively long sludge ages (Eqs. 15 and 16). All solids fractions are in terms of VSS. The equation expressing the accumulation of endogenous residue is based on the nett effect observed (Eq. 18). The equation for the accumulation of the inert solids, X_i, is due to McKinney and Ooten (1969).

A number of parameters are to be determined:

(1) Active mass: i.e. the nett live mass as a result of both synthesis of live mass from COD and loss of live mass due to endogenous respiration.

(2) Endogenous residue mass: approximately 20 per cent of the nett live mass that disappears due to endogenous respiration remains as unbiodegradable volatile organic material.

(3) Inert mass: the influent may contain unbiodegradable volatile solids. If the sludge age is longer than the hydraulic retention time, these solids accumulate in the reactor to a value greater than that in the influent.

(4) Oxygen consumption: oxygen is required for synthesis and endogenous respiration during carbonaceous energy utilization, also for oxidation of ammonia. Ammonia oxidation will be considered separately at a later stage.

A diagramatic sketch of the process is given in Fig. 3. This sketch differs from that usually presented in that the sludge wasted per day is abstracted directly from the reactor; the usual practice is that the waste sludge is abstracted from the secondary settler underflow. It will be shown at a later stage that sludge wastage via the underflow suffers from certain practical disadvantages in process control. System equations incorporating abstraction from the underflow is set out by Lawrence and McCarthy (1970).

The sludge age, R_s, in days, is defined by

$$R_s = \frac{\text{mass of sludge in reactor}}{\text{mass of sludge wasted per day}} \quad \text{(days)} \qquad (21)$$

By abstracting the sludge directly from the reactor, the wasted liquor and reactor liquor concentrations are the same. If a sludge age of, say, 10 days is required, one tenth of the volume of the reactor must be wasted every day. This can be achieved by a constant draw off at flow rate, q, per day where q.1 = v, the volume to be wasted, hence

$$R_s = \frac{XV}{Xv} = \frac{XV}{Xq} = \frac{V}{q} \qquad (22)$$

Three mass balances are now made on (1) active volatile solids, X_a, (2) endogenous residue solids, X_e, and (3) substrate, S.

Balance on X_a: change in the mass of active volatile solids in the reactor is due to (a) sludge synthesis, Eq. (16), (b) endogenous mass loss, Eq. (17) and (c) sludge abstraction.

$$VdX_a = (YKSX_a)Vdt - (bX_a)Vdt - qX_a dt \qquad (23)$$

Balance on S: change is due to (a) sludge synthesis, Eq. (15), (b) influent flow and (c) effluent and sludge abstraction flows.

$$VdS = -(KSX_a)Vdt + S_iQdt - Sqdt - S(Q - q)dt$$

$$= -(KSX_a)Vdt + S_iQdt - SQdt \qquad (24)$$

Balance on X_e: change is due to (a) endogenous mass generation, Eq. (18) and (b) sludge abstraction

$$VdX_e = 0{,}2\ bX_aVdt - qX_edt \qquad (25)$$

At steady state

$$\frac{dX_a}{dt} = \frac{dS}{dt} = \frac{dX_e}{dt} = 0 \qquad (26)$$

In Eqs. (23 to 25) divide by Vdt and equate to zero. Note also that V/q = R_s and V/Q = R. Eqs. (23 to 25) become respectively

$$YKSX_a - X_a/R_s - bX_a = 0 \qquad (27)$$

$$-KSX_a + S_i/R - S/R = 0 \qquad (28)$$

$$0{,}2bX_a - X_e/R_s = 0 \qquad (29)$$

Solving for S, from Eq. (27)

$$S = \frac{1 + bR_s}{YKR_s} \qquad (30)$$

This equation determines the effluent quality. Note that S is independent of R and S_i, being a function only of the sludge age, R_s.

Solving for S, from Eq. (28)

$$S = \frac{S_i}{1 + KRX_a} \qquad (31)$$

Solving for X_e, from Eq. (29)

$$X_e = 0{,}2\ bX_aR_s \qquad (32)$$

Equation (31) contains both X_a and S. It can be transformed to contain X_a only by cross multiplying and substituting for S from Eq. (30), and reducing

$$X_a = \frac{Y(S_i - S)}{1 + bR_s}\frac{R_s}{R} \qquad (33)$$

Oxygen requirements

Oxygen demand is due to (1) synthesis, Eq. (7) and (2) endogenous respiration, Eq. (20)

$$VdO = (1 - 1{,}42Y)QdSdt + 1{,}42.0{,}8bX_aVdt \quad \text{(mg/d)} \qquad (34)$$

At steady state dS = $(S_i - S)$. Divide by V and note that V/Q = R:

$$dO/day \text{ (per } \ell \text{ reactor volume)} = (1 - 1{,}42Y)\ (S_i - S)/R + 1{,}42.0{,}8bX_a \qquad (35)$$

Equations (30, and 32 to 35) form the basis for the design of activated sludge plants.

Mass parameters

Equation (33) contains, R, which firstly is unknown, and secondly its presence tends to imply that this parameter constitutes a basic parameter in the theory. Greater insight into the process behaviour is obtained by considering the masses of X_a, X_e, S_i, S and O.

Let the parameter $MX_a = VX_a$

$MX_e = VX_e$

$M\Delta S = Q(S_i - S)$ and so on.

Multiply Eqs. (32), (33) and (35) by V and noting that R = V/Q:

$$MX_a = \frac{YR_s}{1 + bR_s} M\Delta S \quad \text{(mg)} \qquad (36)$$

$$MX_e = 0{,}2bR_s\ MX_a = \frac{0{,}2(YR_s)\ (bR_s)\ M\Delta S}{1 + bR_s} \quad \text{(mg)} \qquad (37)$$

$$MO/day = (1 - 1{,}42Y)\ M\Delta S + 0{,}8.1{,}42\ bMX_a \quad \text{(mg/d)} \qquad (38)$$

Total volatile solids mass, MX_v, is given by

$$MX_v = Mx_a + MX_e \qquad (39)$$

The volume of the reactor is determined from the value specified for the MLVSS concentration in the reactor, X_v, i.e.

$$V = MX_v/X_v \qquad (40)$$

and the hydraulic retention time R is determined from the flow per day

$$R = V/Q \qquad (41)$$

We arrive at the following important conclusions:

The mass of volatile solids in the reactor is a function only of the mass of COD utilized per day and the sludge age. Consequently, in so far as the mass of sludge is affected, it is immaterial whether the mass of COD utilized arises from a low daily flow with a high COD concentration or a high daily flow with a low COD concentration. Provided $Q(S_i - S)$ is the same in both instances, the masses of sludge will be identical, if the sludge ages are identical. Furthermore, if the concentrations of sludge in the two reactors are specified to be the same, the reactor volumes will be identical. However, the

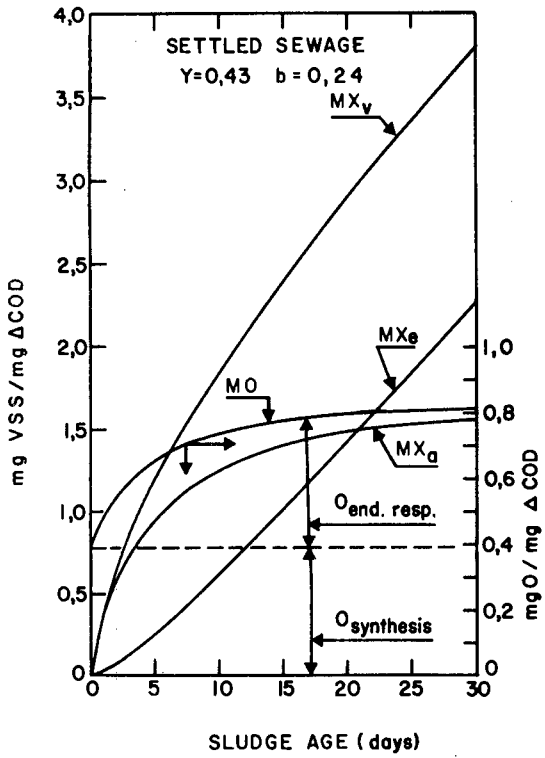

Figure 4
Relationship between the masses of sludge fractions and daily oxygen demand with sludge age in reactor for one mg of COD utilized per day

hydraulic retention times will differ, being long in the first and short in the second instances respectively. The hydraulic retention time, therefore, is incidental on the COD mass utilized, the MLVSS and the daily flow – it serves no basic kinetic function.

Steady state design charts

Plots of Eqs. (36 to 39) are shown in Fig. 4 for $M\Delta S$ = 1 mg COD, Y = 0,43 mg VASS/mg COD removed and b = 0,24 mg VASS/mg VASS/d. The plots in effect give the masses of X_a and X_e that must be contained in the reactor for unit COD utilized per day for sludge ages up to 30 days. Also shown is the associated mass of oxygen to be supplied per day. The volumes of the reactors between different sludge ages will be in direct proportion to the masses MX_v if the mixed liquor concentrations, X_v, are specified to be the same.

The sequence of design will be: Determine (1) S from Eq. (30), (2) $(S_i - S)$, (3) $M\Delta S$/day from $\sum_1^n Q_n (S_i - S)_n dt$ over the day, (4)MX_a, MX_e and MO/d from Eqs. (36), (37) and (38) respectively, and (5) MX_v from Eq. (39), (6) specify X_v and determine V from Eq. (40) and finally (7) determine R from Eq. (41).

Under normal conditions, a plant receives a daily cyclic varying flow and COD concentrations, i.e. a daily cyclic COD mass load. The steady state equations are strictly no longer valid. However, S (Eq. 30) shows small daily variation, similarly MX_a and MX_e at sludge ages greater than about 5 days. Accepting these approximations, it is allowable to use Eqs. (36) to (38). To use these equations MS_i for the day is calculated from a plot of S_iQ over the day and hence $M\Delta S$ is estimated by assuming a constant value for S in $(S_i - S)$. The oxygen demand will show marked daily cyclic variation. The reason for this is that synthesis takes place very rapidly so that as the influent COD mass varies, concomitantly the mass oxygen demand for synthesis will vary. In contrast, the oxygen demand for endogenous respiration remains virtually constant over the day because the variation of MX_a over the day is negligibly small. If the maximum equivalent COD load per day at any time during the day is x times the average, the corresponding maximum carbonaceous oxygen demand is approximated by

$$MO/day\ (max) = x(1 - 1{,}42Y)M\Delta S + 0{,}8.1{,}42\ bMX_a \quad (42)$$

This procedure will usually significantly overestimate the carbonaceous oxygen demand and constitutes a very conservative estimation procedure for design. The reason for this is that the storage of COD on the organism (which precedes COD metabolism) has been neglected. This attenuates the peak oxygen demand to a considerable degree. Incorporation of the storage effect during cyclic load conditions is considered in the following paper.

COD fractions

Experimentally the proportion of COD in the liquid and particulate phases of an unsettled municipal sewage is approximately in the proportion of 40:60 (see Fig. 5). The primary settling tank removes only a fraction of the particulate phase so that even in settled sewage the major portion of COD is still in the particulate phase, in a relatively stable emulsified form. Consequently from a biodegradability point of view settled sewage does not differ appreciably from unsettled sewage; characterization based on this division is unproductive.

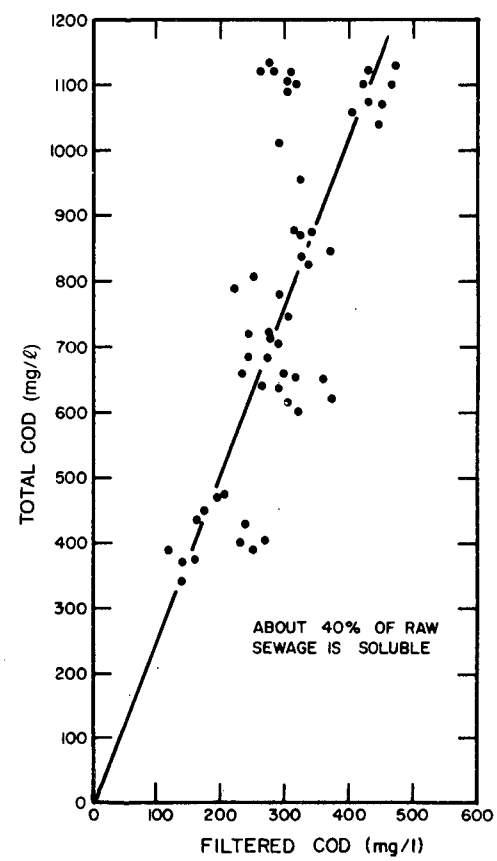

Figure 5
Relationship between soluble and total COD in raw sewage influent from Strandfontein sewer, Cape Town

A useful division is separation into biodegradable and unbiodegradable fractions. Both these fractions contain soluble and particulate COD. Insofar as the biodegradable COD is concerned, no distinction is made between the particulate and soluble COD, as both are apparently equally amenable to biological degradation. However, in the unbiodegradable fraction, the soluble and the particulate COD must be kept separate, as the former is discharged with the effluent whereas the latter accumulates in the sludge mass and is discharged during daily sludge wastage.

Define the influent COD fractions as follows:

S_o = Total COD (mg/ℓ)
S_i = Biodegradable COD (mg/ℓ)
S_u = Unbiodegradable soluble COD (mg/ℓ)
S_{xii} = Unbiodegradable particulate COD (mg/ℓ)

Then:

$$S_i = S_o - S_u - S_{xii} \quad (43)$$

It is convenient to express S_u and S_{xii} empirically in terms of S_o.

Unsettled Sewage

$$S_u = (0{,}05 \text{ to } 0{,}07)\ S_o \quad (44)$$

$$S_{xii} = (0{,}09 \text{ to } 0{,}13)\ S_o \quad (45)$$

Settled Sewage

$$S_u = (0{,}06 \text{ to } 0{,}12)\ S_o \quad (46)$$

$$S_{xii} = 0 \quad (47)$$

These values are based on data from laboratory scale activated sludge plants treating effluents from four different municipal sources. The variability of wastewaters is such that it is difficult to give smaller ranges. Generally the fraction S_u tends to increase if industrial wastes are present in the influent.

The unbiodegradable influent solids, X_{ii}, are found from S_{xii} as follows

$$X_{ii} = S_{xii}/1{,}42 \quad (48)$$

Accumulation of X_i in the reactor is found from a mass balance (see Fig. 3)

$$VdX_i = X_{ii}Qdt - X_iqdt.$$

Dividing by V, equating to zero for steady state and noting that

$$V/q = R_s \text{ and } V/Q = R$$

$$X_i = X_{ii}\,R_s/R \quad \text{and} \quad (49)$$

$$MX_i = MX_{ii}R_s \quad (50)$$

The total volatile solids is now given by

$$X_v = X_a + X_e + X_i \quad (51)$$

$$MX_v = MX_a + MX_e + MX_i \quad (52)$$

Once the biodegradable COD, S_i, is known the equations developed earlier are valid and S, X_a, X_e and O can be calculated.

Effluent COD is given by

$$S_{ef} = S + S_u \quad (53)$$

and if volatile solids X_{ef} are present in the effluent

$$S_{ef} = S + S_u + 1{,}42X_{ef} \quad (54)$$

In design the following sequence of calculation is suggested: Determine (1) S_{xii} (Eq. 45 or 47), S_u (Eq. 44 or 46), X_{ii} (Eq. 48), (2) S_i (Eq. 43), (3) S (Eq. 30), (4) $M\Delta S$, (5) MX_a, MX_e and MX_i (Eqs. 33, 32 and 50) respectively, hence MX_v (Eq. 52), (6) MO/d (Eq. 38), (7) V (Eq. 40), (8) R (Eq. 41) and (9) S_{ef} (Eq. 53 or 54).

Functional inter-relationships

A number of equivalent forms are listed below, also some functional inter-relationships at present still used in design.

$$MX_a = \frac{YR_s.M\Delta S}{1 + bR_s} \quad (55a)$$

$$MX_e = 0{,}2\ bR_sX_a = \frac{YR_s.M\Delta S.0{,}2\ bR_s}{1 + bR_s} \quad (55b)$$

$$MX_v = MX_a + MX_e = \frac{YR_s.M\Delta S}{1 + bR_s}.\ (1 + 0{,}20\ bR_s) \quad (55c)$$

$$\text{Active fraction} = MX_a/MX_v = 1/(1 + 0{,}2\ bR_s) \quad (55d)$$

Substrate Utilization Rate (SUR) = Load Factor = Food/micro-organism ratio mg COD/mg MLVSS/d (56a)

$$= \frac{(S_i - S)Q}{X_vV} = \frac{(S_i - S)}{X_vR} \quad (56b)$$

$$= M\Delta S/MX_v \quad (56c)$$

$$= \frac{1 + bR_s}{(1 + 0{,}2\ bR_s)\ YR_s} \quad (56d)$$

Sludge produced/unit COD utilized/day

$$= MX_v/R_s/M\Delta S \quad (57a)$$

$$= M\Delta X_v/M\Delta S \quad (57b)$$

$$= \text{mg } \Delta\text{MLVSS/mg } \Delta\text{COD/d} \quad (57c)$$

$$= \frac{Y(1 + 0{,}2\ bR_s)}{1 + bR_s} \quad (57d)$$

$$= 1/(SUR.R_s) \quad (57e)$$

= sludge wasted/day/unit COD utilized/day

Mass oxygen/day

$$= MO/d \quad (58a)$$

$$= M\Delta S\ (1 - 1{,}42Y) + 0{,}8.1{,}42\ bMX_a \quad (58b)$$

$$= M\Delta S\left[(1 - 1{,}42Y) + 0{,}8.1{,}42\ \frac{bYR_s}{(1 + bR_s)}\right] \quad (58c)$$

$$= M\Delta S\left[1 - 1{,}42Y\ \frac{(1 + 0{,}2\ bR_s)}{(1 + bR_s)}\right] \quad (58d)$$

$$= M\Delta S - 1{,}42\ MX_v/R_s \quad (58e)$$

$$= M\Delta S - 1{,}42\ M\Delta X_v \quad (58f)$$

All these equations exhibit one feature in common that, the various parameters are all functions of the sludge age, which

illustrates the basic nature of this parameter in the process. In fact, once $M\Delta S$ and R_s are specified all the other parameters can be determined directly. Equations (58b and c) express the oxygen demand as the sum of the synthesis and endogenous respiration requirements, whereas Eqs. (58 d, e, f) express the demand as COD utilized less the COD equivalent of the sludge wasted per day (see Fig. 4). The second method of expression is not as informative as the first.

Equations (55 a, b and 58 b, c, d) are general provided $\Delta S = S_i - S$ is used. Equations (58 e, f) apply correctly only for $(S_i - S)$ and settled sewage, i.e. where inert volatile solids are not present in the influent. If X_{ii} is present in the influent $\Delta S = (S_o - S)$ as S_o includes S_{xii} and $MX_v = MX_a + MX_e + MX_i$. The form $(S_i - S)$ applies only if $X_v = X_a + X_e$. For this reason it is recommended that Eqs. (58 a, b, c, d) only be used.

Nutrient requirements for biological synthesis

All biological matter contains fractions of nitrogen and phosphorus. In biological material usually present in the activated sludge process, the fraction nitrogen as N with respect to VSS ranges between 9 and 12 per cent, average of about 10 per cent. Let

f_n = fraction of nitrogen as N in X_a, X_e and X_i

then

f_n = 0,1 mg N/mg VSS.

Similarly the fraction of phosphorus as P with respect to VSS ranges from 2 to 4 per cent, average about 2,5 per cent. Let

f_p = fraction of phosphorus as P in X_a, X_e and X_i

then

f_p = 0,025 mg P/mg VSS

From Eq. (52), the mass of VSS is given by

$$MX_v = MX_a + MX_e + MX_i$$

Sludge wasted per day is MX_v/R_s and a fraction of f_n of this is nitrogen as N. The nitrogen requirement for the process, i.e. the minimum mass of nitrogen as N in the influent fed per day for the process to operate correctly, is equal to the mass of N wasted in the sludge.

Let ΔN = concentration of N (mg N/ℓ) in the influent which is incorporated in the sludge mass, then

Mass of N removed from influent = mass wasted in sludge

$$Q\Delta N = f_n MX_v/R_s$$

$$= f_n \left[\frac{Y(S_i - S)R_s}{1 + bR_s} \cdot (1 + 0{,}2\, bR_s) + X_{ii}R_s \right] \frac{Q}{R_s}$$

i.e.

$$\Delta N(mg/\ell) = f_n \frac{Y(S_i - S)}{1 + bR_s} (1 + 0{,}2\, bR_s) + f_n X_{ii} \qquad (59)$$

Similarly the minimum phosphorus concentration necessary in the influent is given by

$$P(mg/\ell) = f_p \frac{Y(S_i - S)}{1 + bR_s} (1 + 0{,}2\, bR_s) + f_p X_{ii} \qquad (60)$$

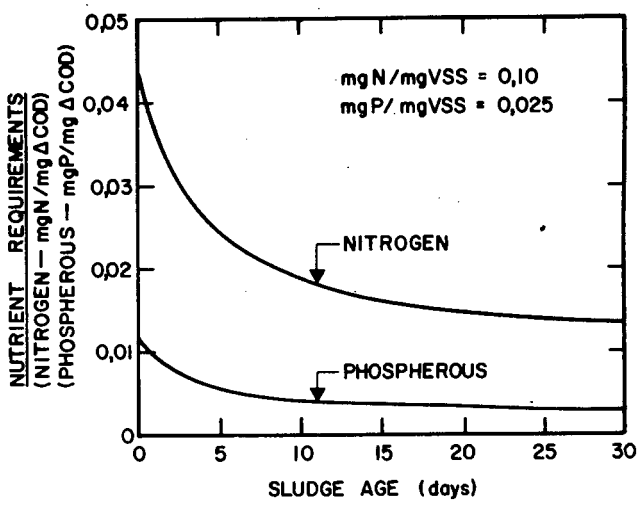

Figure 6
Nutrient requirements per mg of COD utilized per day versus sludge age in the activated sludge process

It is customary to express nutrient requirements in the form COD : N : P = 100 : x : y. In Eqs. (59 and 60) substituting COD = 100, Y = 0,43, b = 0,24 X_{ii} = 0, f_n = 0,1 and f_p = 0,025 then ΔN and ΔP can be plotted versus R_s (Fig. 6). It is evident that as the sludge age increases the nutrient requirements decrease because the net sludge production decreases. This has led to the well known adage "one can always substitute sludge age for nutrient requirements".

Aerobic Digestion

Sludge entering an aerobic digestor can be characterized by division into two fractions: (1) inert and (2) active fractions. Both of these can be measured in terms of either the volatile settleable solids (VSS) or total settleable solids (TSS). During digestion one may assume that the inert mass in the influent to the digestor remains unaffected; the active mass reduces by endogenous respiration and gives rise to two ancillary effects: (1) generation of unbiodegradable settleable solids (endogenous residue) of about 20 per cent of the active mass that disappears and (2) oxygen demand for endogenous respiration.

The problems facing the designer are: (1) what are the active and inert masses in the digestor influent? (2) At what rate does the active mass disappear? (3) What is the oxygen demand rate? The answer to these questions is expedited by establishing a model of the behaviour of the digesting materials. Assume that:

1. Inert solid material in the influent is unaffected by digestion.
2. Active volatile mass degrades according to Eq. (17).
3. A fraction, f, of the active mass which disappears, remains as unbiodegradable solid material, according to Eq. (18).

The mass of sludge is defined by the VSS instead of the TSS. Both can be used if VSS/TSS remains constant but often the ratio changes, particularly if nitrification occurs.

Let

X_a = active solids concentration (mg/ℓ)
X_i = inert solids concentration (mg/ℓ)

X_e = endogenous residue solids concentration (mg/ℓ)
X_v = total solids concentration (mg/ℓ) = $X_a + X_i + X_e$
i,t = further subscripts referring to influent and time respectively
f = fraction $\Delta X_e/\Delta X_a$, usually 0,2
b = nett specific endogenous respiration rate (mg VASS/mg VASS/d).

Batch Digestion

Generally

$$X_{vt} = X_{at} + X_{et} + X_{it} \quad (61)$$

Only X_a and X_e are affected by digestion, X_i remains constant and equal to X_{it}.

Active mass, X_a

$$dX_a/dt = -bX_a \quad (62)$$

which has the solution

$$X_{at} = X_{ae}e^{-bt} \quad (63)$$

Endogenous mass, X_e

Every unit of X_a that disappears generates f units of X_e, i.e.

$$X_{et} = f(X_{at} - X_{at})$$

From Eq. (63):

$$X_{et} = f(X_{at} - X_{at}e^{-bt}) \quad (64)$$

Substituting for X_{at} and X_{et}, from Eqs. (63 and 64) in Eq. (61) and reducing

$$X_{vt} = (1 - f)X_{at}e^{-bt} + fX_{at} + X_i$$

i.e.

$$X_{vt} - X_i - fX_{at} = (1 - f)X_{at}e^{-bt} \quad (65)$$

As $t \rightarrow \infty$, $e^{-bt} \rightarrow 0$ and

$$X_{vt\infty} = X_i + fX_{at} = C \quad (66)$$

where C is a constant value. Substituting for $(X_i + fX_{at})$ from Eq. (66) in Eq. (65)

$$(X_{vt} - C) = I_t = (I - f)X_{at}e^{-bt} \quad (67)$$

Equation (67) implies that if some constant concentration, C, is subtracted from each value of X_{vt}, the balance I is a function solely of X and t. The inter-relationships between the variables are shown in Fig. 7 for b = 0,24 and f = 0,2.

Being an exponential expression Eq. (67) plots linearly when log I_t plotted versus t (on semi-log paper). The slope defines b and the intercept on the I axis, I_o, gives a measure of the active mass:

$$I_o = (1 - f)X_{at}$$

hence

$$X_{ai} = I_o/(1 - f) \quad (68)$$

Knowing X_{at}, the value of X_{it} is determined from the condition at time t = O, i.e.

$$X_{vi} = X_{at} + X_{it} \quad (69)$$

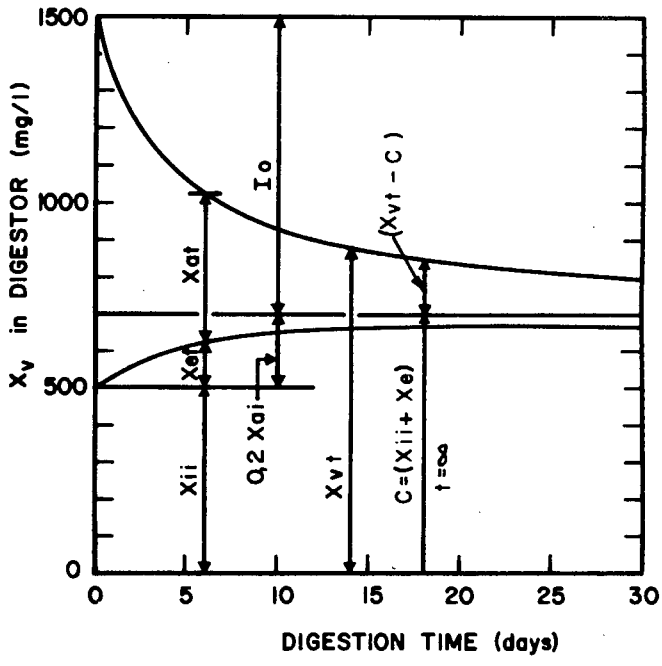

Figure 7
Relationships between the various fractions of volatile solids versus sludge age in aerobic batch digestion of MLVSS

Determination of b using volatile solids

The inter-relationships expressed by Eq. (67) provides an experimental procedure to determine X_{at} and b: In a batch test, a series of X_{vt} values are obtained over a period of time from, say, t = 0 to t = 30 days. A value for C is estimated and subtracted from X_{vt} and the balance plotted log $(X_{vt} - C)$ versus time t. If C is too large, the plot curves downwards, if too small it curves horizontally. Eventually when the best straight line is obtained, the slope is given by

$$b = 2{,}3\frac{\log_{10}(X_{vt1} - C) - \log_{10}(X_{vt2} - C)}{t_1 - t_2} \quad (70)$$

and X_{at} and X_{it} obtained from Eqs. (68) and (69) respectively.

The inter-relationships between the various variables are shown in Fig. 7.

This method gives rise to a very unreliable estimation of b due to the difficulty of measuring X_v reasonably accurately.

Determination of b using oxygen utilization rates

An alternative procedure to determine b can be developed by measuring the rate of oxygen utilization (dO/dt). Now,

$$dO/dt = 1{,}42\ (1 - f)\ bX_{at} \quad (71)$$

but $X_{at} = X_{ai}e^{-bt}$, therefore

$$dO/dt = 1{,}42\ (1 - f)\ bX_{ai}e^{-bt} \quad (72)$$

Taking logs of Eq. (72)

$$\log\ (dO/dt) = \log\ (1{,}42[1 - f]bX_{ai}) - bt\ \log_{10}e \quad (73)$$

which is of the form

$$y = a + b't \quad (74)$$

Hence, plotting log (dO/dt) versus time, the slope equals $-b'$ and b = 2,3b. The intercept on the dO/dt axis, at t = 0 gives:

$$(dO/dt)_i = 1,42\ (1 - f)\ bX_{ai} \quad (75)$$

Having determined b from the slope and reading off $(dO/dt)_i$, one may solve for X_{ai}.

This procedure assumes no nitrification. If there is nitrification Eq. (72) must be augmented by adding the term 0,1.4,6 (1 – f) $bX_{ai}e^{-bt}$ to give

$$dO/dt = (1,42 + 0,1.4,6)\ (1 - f)\ bX_{ai}e^{-bt} \quad (76)$$

It is clear that estimation of b is not affected by nitrification but the estimation of X_{ai} will be. However, care must be taken that during the experiment the pH does not drop below 6 as this may completely stop nitrification.

Completely mixed reactor – single reactor

Usually aerobic digestors are of the flow through completely mixed type, i.e. R = R_s. Doing mass balances over the reactor for active endogenous and inert masses gives

Active mass

$$VdX_a/dt = X_{ai}Q - X_aQ - bX_aV \quad (77)$$

i.e.

$$dX_a/dt = dX_{ai}/R - X_a/R - bX_a \quad (78)$$

At steady state $dX_a/dt = 0$ and

$$X_a = \frac{X_{ai}}{1 + br} \quad (79)$$

Endogenous residue

$$VdX_e/dt = f\,bX_aV - X_eQ \quad (80)$$

at steady state

$$X_e = f\,bX_aR = f(X_{ai} - X_a) \quad (81)$$

Inert mass

$$VdX_i/dt = X_{ii}Q - X_iQ \quad (82)$$

at steady state for a flow through reactor

$$X_i = X_{ii} \quad (83)$$

i.e. the inert influent material remains unchanged.

Total inert mass in effluent, X_{if}

The total inert mass in the effluent from the digestor, X_{if} will be

$$X_{if} = X_{ii} + X_e = X_{ii} + f(X_{ai} - X_a) \quad (84)$$

Total volatile mass in effluent, X_{vf}

$$X_{vf} = X_{if} + X_a \quad (85)$$

Oxygen Demand

Oxygen is required for oxidation of the carbonaceous material, MO/d, plus nitrification, MO_n/d. From Eq. (38), with MΔS = 0 MO/d = 1,42 (1 – f) b MX_a (86)

Nitrification oxygen demand if found by assuming complete nitrification of the TKN released back into the liquid during endogenous respiration. One mg of NH_3–N requires 4,6 mg oxygen, and each mg of X_a contains 0,1 mg NH_3–N, i.e.

$$MO_n/d = 4,6.0,1.(1 - f)b\ MX_a \quad (88)$$

Hence total oxygen demand, MO_T/d,

$$MO_T/d = (1,42 + 0,1.4,6)\ (1 - f)b\ MX_a \quad (88)$$

$$= 1,50\ b\ MX_a \quad (89)$$

Note that the nitrification demand is about 24 per cent of the total demand.

Completely mixed reactors in series

Assume the reactors have the same retention times. If the retention times differ the appropriate equations can be written down immediately from the development below. Consider two digestors in series, designated 1 and 2.

Active mass

$$X_{a1} = \frac{X_{ai}}{1 + bR} \quad (90)$$

$$X_{a2} = \frac{X_{a1}}{1 + bR} = \frac{X_{ai}}{(1 + bR)^2} \quad (91)$$

Endogenous residue

$$X_{e1} = fbRX_{a1} \quad (92)$$

$$= (X_{ai} - X_{a1})f \quad (93)$$

$$X_{e2} = fbRX_{a2} + X_{e1} \quad (94)$$

$$= (X_{a1} - X_{a2})f + (X_{ai} - X_{a1})f$$

$$= (X_{ai} - X_{a2})f \quad (95)$$

The volatile solids in the effluents will be

$$X_{v1} = X_{a1} + X_{e1} + X_{ii} \quad (96)$$

$$X_{v2} = X_{a2} + X_{e2} + X_{ii} \quad (97)$$

Design charts

Once X_{ai} to the digestor is known, either from a theoretical calculation using the kinetic equations for the activated sludge process, or, from a batch experiment using oxygen utilization rates, a decision has to be made as to what level the X_{ai} must be reduced. Reduction by single and series digestion can be readily compared by plotting Eqs. (90 and 91) with log (X_{a1} and X_{a2}) versus total retention time i.e. R and 2R respectively. Fig. 8 shows plots giving the percentage reductions possible for b = 0,24, f = 0,2.

The plots for Fig. 8 show some interesting relationships. If, for example, a straight line is drawn from the origin through the curve depicting the single digestor at R = 7,5 days, it intersects the two digestor curves at 15 days. The first intersection gives the percentage of X_{ai} remaining after 7,5 days digestion (35,7 per cent), the second the percentage of X_{ai} remaining after 15 days digestion, i.e. (7,5 + 7,5) days in the two digestors in series (12,6 per cent). This last value is to be compared with the percentage remaining after digestion in a single digestor for 15 days retention time (21,7 per cent). By using two digestors

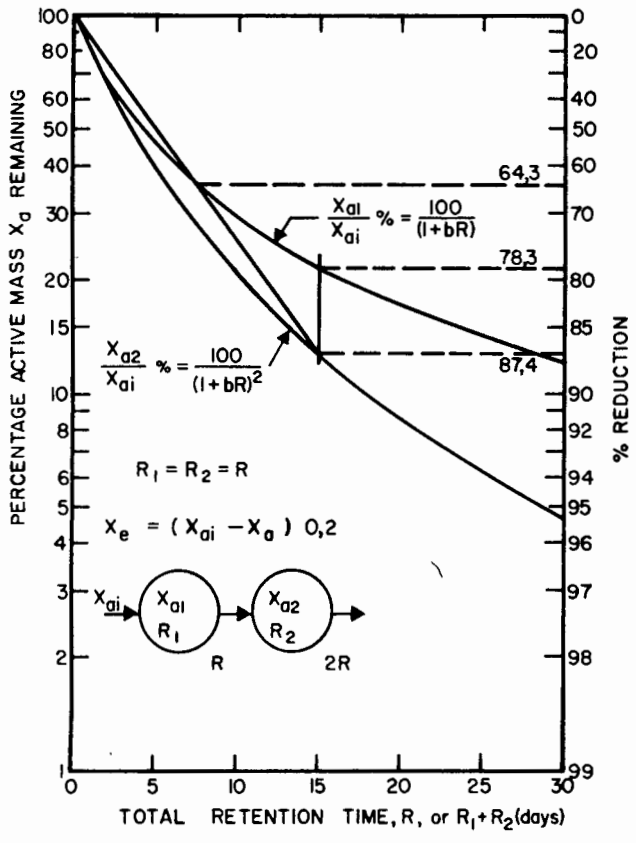

Figure 8
Reduction of active volatile mass in single and two stage flow through aerobic batch digestion of activated sludge

in series each with 7,5 days retention the active material from the series will be half that from a single digestor with 15 days retention. To obtain 12,6 per cent remaining from a single digestor will require a retention time of approximately 28,6 days.

The increase in the NO_3–N concentration in the effluent from a digestor is given by

$$\Delta(NO_3\text{–}N) = (X_{ai} - X_{af})\ (1 - f)f_n\ (mg/\ell) \qquad (98)$$

where $(1 - f) = 0,8$ and $f_n = 0,1$.

Assume a sludge age of 10 days in the activated sludge plant, then for b = 0,24 from Eq. (55d) $X_a/X_v = 0,68$. If the wasted sludge is concentrated to say 3 per cent X_{ai} = 0,68*30 000 = 20270 mg/ℓ. Assuming 15 days retention in a single digestor, from Eq. (90), X_a = 4400 and the nitrate in the effluent, from Eq. (98), $\Delta(NO_3\text{–}N)_a$ = 1270 mg/ℓ. For every molecule of NO_3^- formed a molecule of H^+ is generated i.e. 1 270/14 = 91 millimoles/ℓ of hydrogen ions are formed, i.e. an acidity of 91 × 50 = 4 550 mg/ℓ as $CaCO_3$ is generated and must be neutralized by at least 4 550 mg/ℓ of $Ca(OH)_2$ as $CaCO_3$. Otherwise the pH will drop to very low values and stop nitrification.

The phosphorus released by the digestor will be

$$\Delta(PO_4 - P) = (X_{ai} - X_{af})\ (1 - f)\ f_p$$

where f_p = 0,025. In the example above $\Delta(PO_4 - P)$ = 320 mg/ℓ. If the sludge contains an augmented concentration of phosphorus due to enhanced biological removal of P then the $\Delta(PO_4 - P)$ value could be up to ten times higher. The supernatant from the digestor must be treated with $Ca(OH)_2$ to precipitate the P.

The nitrate can be removed by incorporating a dentrification anoxic reactor in the digestor system (See Appendix B).

Temperature Effects

There appears to be a general acceptance that the yield constant Y is unaffected by temperature although no conclusive supporting experimental evidence could be found in the literature. The endogenous respiration constant and the substrate utilization constant K are temperature dependent, and often are taken to be temperature dependent to the same degree. It is difficult to identify the "best" values for the temperature dependency as past research did not formulate the dependency in terms of the active endogenous fraction in the sludge.

The usual form for the temperature dependency is the simplified Arrhenius equation, for example for the endogenous rate constant, b,

$$b_T = b_{20}\ \theta^{T-20} \qquad (99)$$

where b_T = value at T°C
b_{20} = value at 20°C
θ = constant
T = temperature in deg. C.

Experimental data for b, reported later in this paper, gives b_T = 0,24 $(1,029)^{T-20}$ (100)

This value for θ is accepted also for K, i.e.

$$K_T = 0,07\ (1,029)^{T-20} \qquad (101)$$

Nitrification

Nitrification is the biological process whereby nitrogen present as free and saline ammonia is converted into nitrites and nitrates. The nitrogen content of wastewater is expressed in terms of N, the nitrogen atom. Thus, ammonia as nitrogen, written $(NH_3\text{–}N)$ = 30 mg/ℓ implies an ammonia concentration containing 30 mg/ℓ of N.

There are two principal forms of ammoniacal nitrogen (1) free and saline ammonia present in NH_3 (dissolved) and NH_4^+ (ionic) forms the fractional division of the two forms being a function only of the pH. (2) Organic bound ammonia in which the NH_4^+ radical is bound to a carbonaceous molecule to form a proteinaceous substance.

The free and saline ammonia is measured by a test of this name. The Total Kjeldhal Nitrogen (TKN) test measures both the free and saline and organic bound ammonia so that the organic bound ammonia is found from the difference of these two test values. All experimental nitrogen values in this investigation were determined by the TKN test. This procedure was followed as there is continuous conversion in the process from the bound ammonia to the free and saline form and it was preferable to link the NH_3 form to the TKN rather than to deal with the NH_3 form independently.

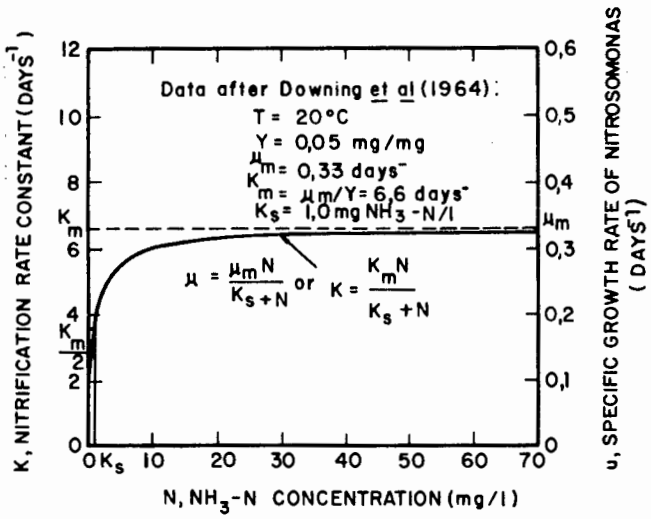

Figure 9
Monod's relationship for nitrification at 20°C

Nitrification stoichiometry

Nitrification occurs in two steps:

1. $NH_3 \rightarrow NO_2$ (Nitrosomonas)
2. $NO_2 \rightarrow NO_3$ (Nitrobacter)

The stoichiometric reactions are:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ \quad (102)$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \quad (103)$$

$$2NH_4^+ + 4O_2 \rightarrow 2NO_3^- + 2H_2O + 4H^+ \quad (104)$$

From Eq. (104) 4 moles of O_2 are required to convert 2 moles of NH_3 to NO_3^-

i.e.
1 (NH_3–N) mole requires 2 moles O_2
i.e.
1.14 mg N requires 2.32 mg O_2
i.e.
1 (NH_3–N) mg/ℓ requires 2.32/14 = 4,6 mg/ℓ O_2
i.e.
4,6 mg/ℓ O_2 is required for nitrification of 1 mg/ℓ (NH_3–N).

In the nitrification process the nitrosomonas is the slowest reacting organism. Consequently it is not common to have NO_2^- in the effluent as the nitrobactor will rapidly convert the NO_2^- to NO_3^-.

Basic nitrification kinetics

In conformity with Eq. (10) one can write

$$\frac{dX_n}{dt} = \mu X_n = \left(\frac{\mu_{nm} N}{K_n + N}\right) X_n \quad (105)$$

where X_n = concentration of nitrosomonas (mg/ℓ)
μ = growth rate of nitrosomonas (mg/mg/d)
μ_{nm} = maximum growth rate (mg/mg/d)
K_n = concentration of (NH_3–N) when $\mu = \frac{1}{2}\mu_{nm}$
N = concentration of (NH_3–N)

According to Downing *et al* (1964) the endogenous respiration rate, b_n, is so small that it can be neglected. They give the following values for μ_{nm} = 0,33/d and, K_n = 1,0 mg (NH_3–N)/ℓ at 20°C. In Fig. 9 the relationship between μ and N is depicted. It is evident that the values of μ_{nm} and K_n are such that for N>2 mg/ℓ, μ is practically equal to μ_{nm}. Consequently nitrification takes place at maximum rate at all concentrations of N greater than about 2 mg/ℓ and rapidly falls off if N is below this value.

Minimum process sludge age, R_{sm}

Referring to Fig. 3 doing a mass balance on X_n, neglecting endogenous respiration

$$\frac{VdX_n}{dt} = \left(\frac{\mu_{nm} N}{K_n + N}\right) \frac{X_n V}{z} - X_n q \quad (106)$$

At steady state $dX_n/dt = 0$ and noting that $V/q = R_s$

$$\frac{1}{R_s} = \frac{\mu_{nm} N}{K_n + N} \quad (107)$$

A plot of Eq. (107), N versus R_s is shown in Fig. 10 for μ_m = 0,33 and K_n = 1 mg(NH_3–N)/ℓ. As R_s is reduced N increases until it equals the influent (NH_3–N) concentration, N_i. Any further reduction of R_s will cause nitrification to cease, i.e. the nitrifiying organisms are washed out. Substituting $N = N_i$ in Eq. (107) gives the minimum sludge age R_{sm}, necessary for nitrification. For all values of N_i greater than about 5 mg/ℓ, K_n is negligible with respect to N_i and can be neglected i.e.

$$\frac{1}{R_{sm}} = \frac{\mu_{nm} N_i}{N_i} = \mu_{nm}$$

or

$$R_{sm} = \frac{1}{\mu_{nm}} \quad (108)$$

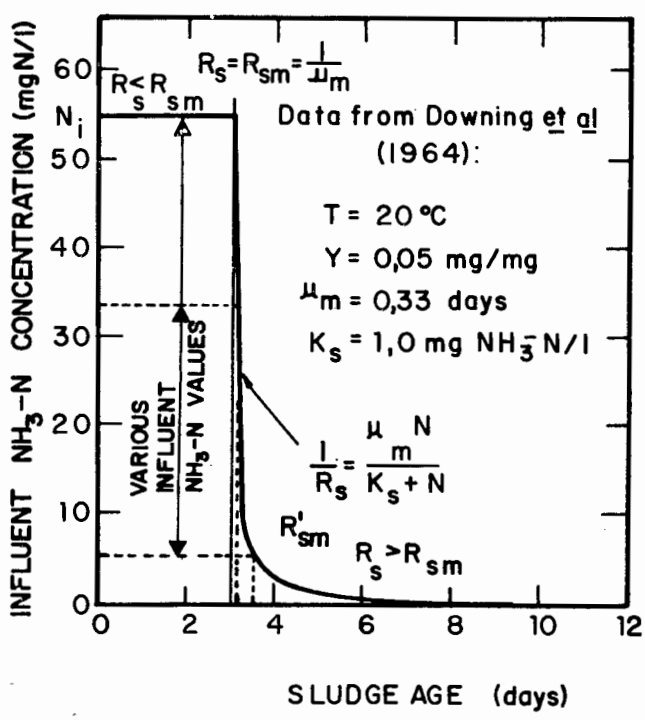

Figure 10
Relationship between sludge age for nitrification and influent (NH_3-N)

Hence if $N_i > 5$ mg/ℓ the value of R_{sm} is virtually independent of N_i, i.e. R_{sm} is constant. As it is unlikely that $N_i > 5$ mg/ℓ in the usual sewage influents, R_{sm} will be constant at a particular temperature. In this fashion one can speak of a minimum sludge age for nitrification.

Factors influencing μ_m and K_n

The following factors influence the growth rate and minimum sludge age requirements of the nitrosomonas.

1. Temperature.
2. pH.
3. Toxic substances.
4. Oxygen concentration.

1. Temperature

The maximum growth rate, μ_{nm}, is significantly affected by temperature. From Downing *et al* (1964) the effect of temperature can be described by

$$\mu_{nmT} = \mu_{nm20}\,\theta^{(T-20)} \qquad (109)$$

$$= 0{,}33\,(1{,}123)^{T-20}\ d^{-1} \qquad (110)$$

As $R_{sm} = 1/\mu_{nm}$, the minimum sludge age, R_{smT}, at temperature T°C is

$$R_{smT} = 3{,}0(1{,}123)^{20-T}\ \text{days} \qquad (111)$$

Thus for every 6 deg C drop in temperature the minimum sludge age is doubled.

Equation (111) was established for domestic wastewaters containing negligible inhibitory substances, in the temperature range 5 to 25°C and for pH values of the MLSS ranging from 7,2 to 8.

2. pH

Downing *et al* (1964) found that μ_{nm} decreases with pH below 7,2 but remained approximately constant in the range pH 7,2 to 8,0. They proposed the following relationship:

$$\mu_{nmpH} = (1 - 0{,}83)\,(7{,}2 - \text{pH})\,\mu_{nm} \qquad (112)$$

where μ_{nmpH} = maximum growth rate at the particular pH
μ_{nm} = maximum growth rate at pH 7,2.

Equation (112) has a restricted range of validity pH 6,0 to 7,2.

Wastewaters having a low buffering capacity, due to low alkalinity, are often encountered where the municipal supply is drawn from areas underlain with sandstone. Nitrification reduces the pH to values often as low as 4 (see Fig. 11). Under such conditions it is difficult to describe the kinetics of the nitrification process, for as the sludge age increases sufficiently to bring about nitrification, the drop in pH increases the minimum sludge age, i.e., there is a complex interaction of the pH, the nitrification rate and minimum sludge age. An example of the effect of pH on nitrification in a completely mixed activated sludge plant treating a low buffered effluent from Somerset West, South Africa, is shown in Fig. 11 (Somerset West is a small non-industrial town). The TKN in the effluent did not drop below 10 mg/ℓ. Both μ_{nm} and K_n appeared to be affected and the kinetic behaviour is approximately described by $\mu_{nm} = 0{,}2$ and $K_n = 4{,}5$ in Eq. (107). These constants are

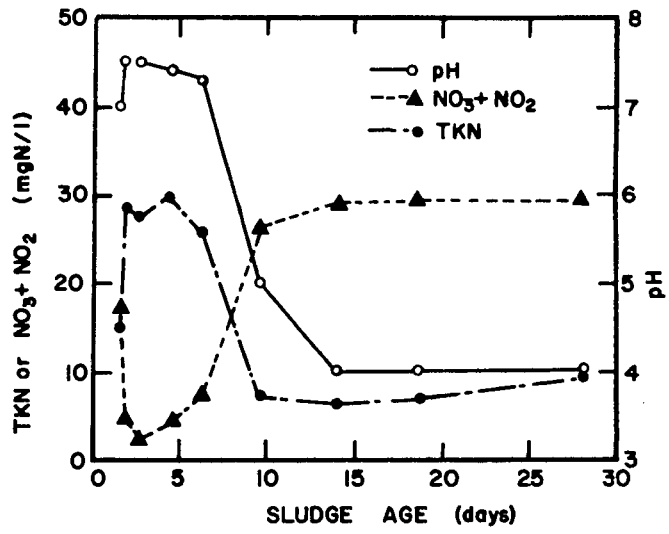

Figure 11
Relationship between TKN, NO_3-N and pH with sludge age in an activated sludge plant treating weakly buffered influent from Somerset West

suspect as the pH changes with the sludge age; in effect a sludge age of approximately 8–10 days was necessary to obtain complete nitrification at 20°C i.e. three times the minimum according to Eq. (111). Subsequently, when the same wastewater was used in a Barnard type nitrification – dentrification process the pH remained at about 7 and nitrification was more complete, the TKN concentration dropping to 4–5 mg/ℓ. Nitrification inhibition was therefore, due to the low buffering capacity of the wastewater and not to toxic inhibition. The favourable influence of dentrification in maintaining the pH near 7 makes a nitrification – dentrification system virtually mandatory for activated sludge treating wastewaters with low alkalinities.

3. Toxic substances

Toxic substances can seriously inhibit the growth of nitrosomonas. Toxic substances usually believed to affect nitrification are the heavy metals chrome, lead and mercury. In Birmingham, where the wastewater contains a high proportion of industrial wastes from the metal finishing industries, μ_{nm} was found to be less than half the value given by Downing (Jenkins *et al*, 1967). It is difficult to pinpoint what substances influence nitrification. The effect of heavy metals is certainly not as severe as is often implied, but other chemicals of an organic nature can completely inhibit nitrification. The problem needs further investigation. It should be noted that despite the heavy metal content of Birmingham sewage nitrification was only slowed down, requiring longer sludge ages, but did not cease.

4. Oxygen concentration

Dissolved oxygen is a prerequisite for nitrification. Downing *et al* (1964) recommends that the dissolved oxygen concentration should not fall below 0,5 mg/ℓ. As the dissolved oxygen concentration varies in parts of the tank, this means that the general level should be kept higher, and particularly during the daily high load period oxygen must be present otherwise nitrification will not take place. Nitrification requires greater surety of oxygen supply than that for carbonaceous removal. In carbonaceous energy removal adsorption, which precedes metabolism, can store energy to a certain degree until oxygen becomes available again. In contrast, nitrification ceases the moment the oxygen drops below the critical level.

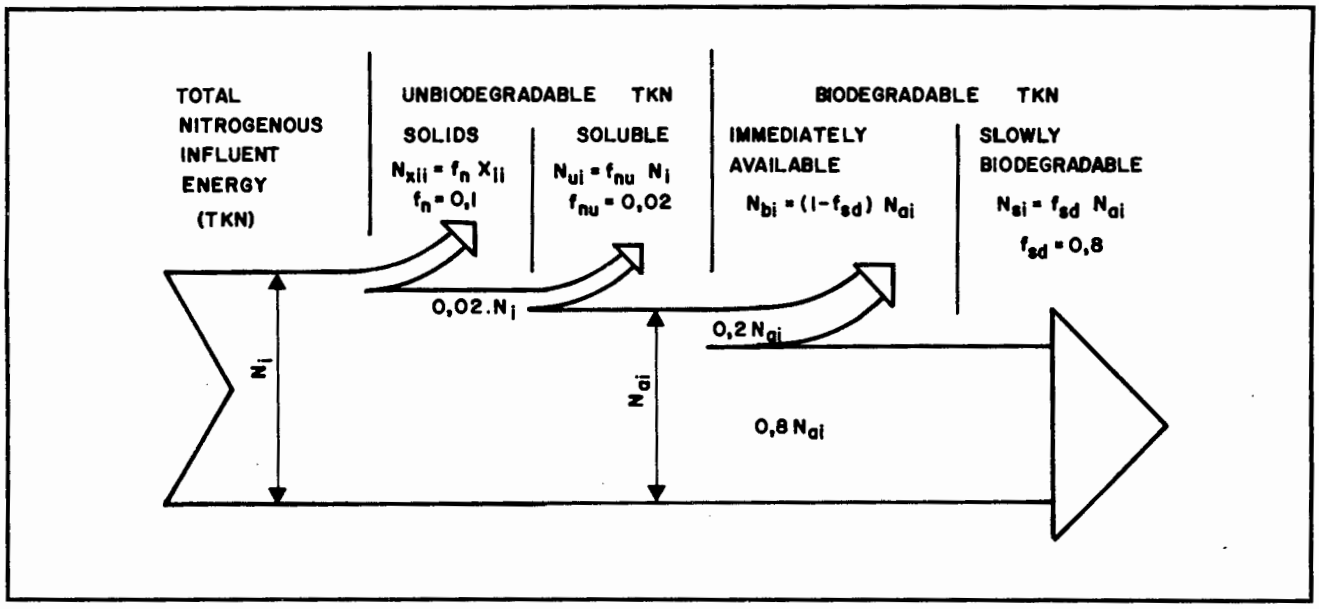

Figure 12
Fractions of TKN in raw sewage influent to activated sludge plant

Influent TKN Fractions

The usual assumption in nitrification kinetics is that all the TKN remaining, after the nitrogen for synthesis has been subtracted, is nitrified. However, from laboratory scale completely mixed activated sludge units receiving a daily cyclic influent flow in the form of a square wave (i.e. a feed period of 12 hours and a non-feed period of 12 hours) showed that nitrification was not complete. During the 12 hr feed period there was a steady increase of TKN and a corresponding steady decrease of nitrate concentration in the effluent. During the 12 hr non-feed period the TKN was slowly reduced and the nitrate slowly increased, indicating that the TKN was being converted to a form that apparently allowed nitrification to occur. It was also noticed that the instant the feed period terminated, the oxygen utilization rate precipitously decreased to a value given by the carbonaceous oxygen demand. This indicated that a fraction of the influent TKN was immediately available for nitrification.

From the analysis of a number of dynamic behaviour patterns it was concluded that the influent TKN consisted of a number of fractions each of which responded in a different manner in the activated sludge process.

The influent TKN, N_i, is divided into two fractions (1) unbiodegradable and (2) biodegradable.

(1) Unbiodegradable influent TKN

The unbiodegradable TKN consists of two fractions (a) soluble unbiodegradable TKN, N_{ui} and (b) particulate unbiodegradable TKN, N_{xii}. The fractions are conveniently linked with the influent TKN, N_i as follows:

$$N_{ui} = f_{nu}N_i \quad (113)$$

$$N_{xii} = f_n X_{ii} \quad (114)$$

where $f_{nu} \approx 0,02$ and $f_n = 0,1$.

(2) Biodegradable influent TKN

The TKN remaining, after the unbiodegradable fraction has been subtracted, constitutes the biodegradable TKN, N_{ai}, i.e.

$$N_{ai} = N_i - N_{ui} - N_{xii} \quad (115)$$

The biodegradable TKN is divided into two fractions (a) slowly biodegradable, N_{si}, and (b) immediately available for nitrification, N_{bi}. These fractions are empirically linked to N_{ai} as follows:

$$N_{si} = f_{sd}N_{ai} \quad (116)$$

$$N_{bi} = (1 - f_{sd})N_{ai} \quad (117)$$

where $f_{sd} \approx 0,8$.

The division of the influent TKN into the various fractions is shown in Fig. 12.

Nitrification process kinetics

Recognition of the presence of a slowly biodegradable TKN, which is not immediately available for nitrification, requires a modification of the normal nitrification theory as applied to process kinetics. The minimum sludge age as set out previously should not be affected, as usually the influent will contain immediately available nitrogen for nitrification in excess of about 5 mg/ℓ. The extent of nitrification however, will be affected as this depends principally on the rate of conversion of slowly biodegradable TKN to immediately available nitrogen. As we have seen the slowly biodegradable nitrogen constitutes a major fraction of the influent TKN, $f_{sd} = 0,8$.

Readily available nitrogen, N_{nh3}

In the steady state process the nitrogen available for nitrification is the balance after the nitrogen concentrations in the reactor due to (1) unbiodegradable soluble from influent, (2) inert volatile particulate from influent, (3) synthesized volatile and

(4) slowly biodegradable nitrogen have been subtracted, i.e.

$$N_{nh3} = N_i - N_u - N_{xi} - N_{syn} - N_s \quad (118)$$

1. Unbiodegradable soluble nitrogen, N_u: Steady state concentration is given by:

$$N_u = N_{ui} \quad (119)$$

2. Nitrogen in inert volatile material in influent, N_{xii}: A mass balance on N_{xi} gives:

$$N_{xi} = N_{xii} = 0{,}1\ X_{ii} \quad (120)$$

3. Nitrogen in synthesized material, N_{syn}: From Eq. (59):

$$N_{syn} = \frac{0{,}1\ Y\ (S_i - S)}{1 + bR_s}\ (1 + 0{,}2\ bR_s) \quad (121)$$

4. Slowly biodegradable nitrogen, N_s: The sources of slowly biodegradable nitrogen are: (a) Influent, i.e. $f_{sd}Q\ N_{ai}$. (b) Lysed material from endogenous mass loss. The dynamic model gave the best correlation with observed behaviour when it was assumed that 80 per cent of the lysed nitrogen was slowly biodegradable, i.e. the same fraction, f_{sd}, as for the influent N_{ai}. As 20 per cent, i.e. fraction, f, of the mass of organisms that die remains as unbiodegradable volatile particulate matter, the slowly biodegradable nitrogen from endogenous mass loss per day is $(1 - f)f_{sd}\ f_n\ bX_aV$. Degradation of slowly biodegradable nitrogen appears to be a first order reaction, i.e.

$$dN_s/dt = k_sN_sX_a \quad (122)$$

where $k_n = 0{,}01$ mg N_s/mg X_a/d.

Performing a mass balance on N_s (Fig. 3):

$$VdN_s = f_{sd}N_{ai}Qdt + f_{sd}(1 - f)f_nbX_aVdt - k_nN_sX_aVdt - N_sQdt \quad (123)$$

At steady state $dN_s/dt = 0$. Dividing Eq. (123) by Vdt, noting $V/Q = R$, equating to zero and solving for N_s.

$$N_s = \frac{f_{sd}[N_{ai} + R(1 - f)f_nbX_a]}{1 + k_nX_aR} \quad (124)$$

Nitrate formation

Equation (105), slightly modified as below, formulates the rate of nitrification, dN/dt, i.e.

$$\frac{dX_n}{dt} = Y_n\frac{dN}{dt} = \frac{\mu_{mn}N}{K_n + N}X_n \quad (125)$$

Based on Eq. (105) the minimum sludge ages necessary for nitrification in the process was developed, Eq. (108). Equation (108) appears to be in reasonable accord with practical observation in so far as the minimum sludge ages are concerned. However, when applying Eq. (125) to determine the nitrogen concentration in laboratory scale activated sludge process units treating raw and settled municipal wastewaters, the maximum rate constant, μ_{nm}, had to be increased by at least an order of magnitude to obtain rates consistent with those observed experimentally. For all practical purposes the conversion of NH_3 to nitrate was immediate. Consequently in this paper the concentration of nitrate in the effluent is taken as equal to the steady state ammonia value (eq. (118)) i.e.

$$NO_{3ef} = N_{nh3} \quad (126)$$

Effluent TKN

Effluent TKN is given by:

$$TKN_{ef} = N_s + N_u + 0{,}1\ X_{vef} \quad (127)$$

Nitrification oxygen demand

Stoichiometrically 1 mg (NH_3–N) requires 4,6 mg/ℓ Oxygen. The daily oxygen demand is thus directly related to the nitrate concentration in the effluent, i.e.

$$MO_n/day = 4{,}6.NO_{3ef}.Q\ mg/d \quad (128)$$

Experimental Investigations

Experimental framework

The theory set out above forms a framework for devising experimental procedures to measure the constant Y, b and K. The difficulties associated with this endeavour are highlighted by a critical review of current methods employed.

Determination of Y and b

A widely used method is based on the relationship linking the Sludge Loading Rate (SLR) and the sludge age, R_s (or, equivalently the sludge growth rate). The SLR was developed in an endeavour to find some parameter giving a measure of the Food/Micro-organism (F/M) ratio. Originally the SLR was defined as

$$SLR = \frac{\text{Mass of substrate applied/day}}{\text{Mass of MLSS}} = \frac{S_oQ}{X_TV} = \frac{MS}{MX_T} = \frac{S_o}{X_TR} \quad (129)$$

Usually the substrate (or energy) was measured in terms of the 5 day BOD.

As a theoretical parameter the SLR has the following disadvantages: (1) the ratio X_v/X_T is not the same between plants due to different degrees of adsorption and precipitation of inorganic salts on to the sludge mass. Hence X_T does not form a consistent parameter with respect to the volatile solids (Heukelekian *et al*, 1951). (2) As defined the SLR cannot be incorporated directly into the theoretical framework of the kinetic theory. In terms of the theory, from Eq. (55c)

$$\frac{(S_i - S)}{X_vR} = \frac{1 + bR_s}{1 + 0{,}2bR_s}.\frac{1}{R_sY} = \frac{M\Delta S}{MX_v} = SUR_v \quad (130)$$

where $X_v = X_a + X_e$

Equation (130) indicates that the "loading rate" should be in terms of the mass of substrate *utilized* instead of the mass of substrate *applied*. The difference between mass of substrate applied and utilized is small if the BOD is used as substrate parameter, because $(S_i - S)/S_i > 90$ percent in the normal range of loading. However if the COD is used as substrate parameter the error in using Eq. (129) can be large as a significant fraction of the influent COD may be unbiodegradable.

In order to eliminate the errors introduced by (1) and (2) above it is now fairly generally accepted that the sludge loading rate should be defined by Eq. (130). To distinguish it from the SLR and to indicate that it is in terms of volatile solids the

following name is suggested – Substrate Utilization Rate, SUR_v.

The SUR_v still does not correctly reflect the F/M ratio as the volatile solids, X_v, include the inert endogenous residue, X_e. Theoretically the F/M ratio is given by $M\Delta S/MX_a$, and is directly derived from Eq. (55a) i.e.

$$F/M = SUR_a = \frac{(S_i - S)Q}{X_a R} = \frac{1 + bR_s}{YR_s} = \frac{1/R_s + b}{Y} \quad (131)$$

and can be written as follows:

$$1/R_s = Y.SUR_a - b \quad (132)$$

This equation is linear in SUR_a. For comparison Eq. (130) can be written in the same form as Eqs. (131 and 132) respectively, i.e.,

$$SUR_v = \frac{1/R_s + b}{Y}\left[\frac{1/R_s}{1/R_s + 0{,}2b}\right] \quad (133)$$

i.e.

$$1/R_s = \left[\frac{1/R_s + 0{,}2b}{1/R_s}\right]Y.SUR_v - b \quad (134)$$

In the current methods of analysis the convention is to utilize Eq. (132) *but to substitute SUR_v for SUR_a*, i.e.

$$1/R_s = Y.SUR_v - b \quad (135)$$

The reason for this usage appears to be that as no procedure existed to identify X_a, the difference between X_a and X_v was simply ignored. The errors introduced in the anlysis of experimental data by using Eq. (135), i.e. substituting SUR_v for SUR_a, can be evaluated as follows: Assume Y and b are known. In Fig. 13 are shown plots of Eqs. (132 and 134), SUR versus $1/R_s$ for Y = 0,43 and b = 0,24. [The determination of these "correct" values of Y and b are discussed later.] The theoretical SUR_a versus $1/R_s$ plot (eq. 132) is linear with slope equal to Y and the intersection on the $1/R_s$ axis equal to b. In contrast the theoretical SUR_v plot (Eq. 134) is curved passing through the origin. Experimental Sur_v values are also shown plotted in Fig. 13, the plots conforming to the SUR_v curve.

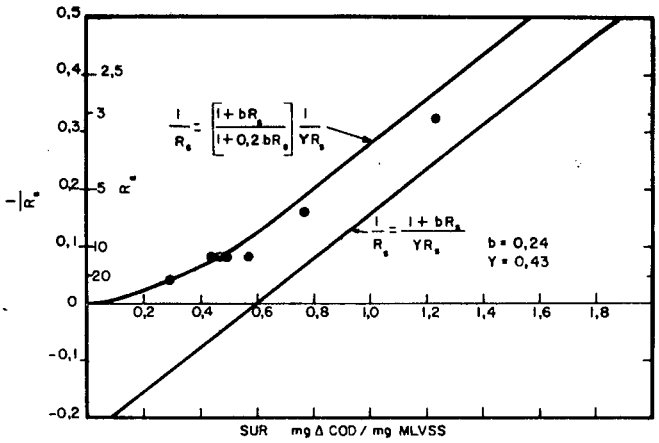

Figure 13
Experimental and theoretical relationships between sludge age and substrate utilization rate

If the current practice is followed, to accept that the experimental plots utilizing SUR_v are linear, i.e. that Eq. (135) applies, then the best straight line is drawn through the experimental data. A value of b is found from the intersection of the straight line with the $1/R_s$ axis. In general this procedure always underestimates b, by at least 50 per cent if the R_s values are low, and up to 90 per cent if the R_s values lie in the range 6 to 30 days. It is due to the use of the incorrect Eq. (135) that such a wide range of b values, and generally such low values have been reported in the literature. It is also due to this procedure that the conclusion has been formed that b decreases as the sludge age increases.

The same problem is present when the constants for oxygen utilization are determined. Here the practice has been to plot MO/MX_v versus SUR_v and to draw the best straight line through the experimental plots, to give a relationship

$$MO/MX_v = a'SUR_v + b' \quad (136)$$

Theoretically the oxygen utilization rate per unit mass of sludge is given by Eq. (58b), i.e.

$$MO/MX_a = (1 - 1{,}42Y)SUR_a + 0{,}8.1{,}42.b \quad (137)$$

or

$$MO/MX_v = (1 - 1{,}42Y)SUR_v + \frac{0{,}8.1{,}42b}{1 + 0{,}2bR_s} \quad (138)$$

Substituting for SUR_a and SUR_v

$$MO/MX_a = (1 - 1{,}42Y)\frac{1 + bR_s}{YR_s} + 0{,}8.1{,}42b \quad (139)$$

$$MO/MX_v = (1 - 1{,}42Y)\frac{1 + bR_s}{(1 + 0{,}2bR_s)YR_s} + \frac{0{,}8.1{,}42b}{1 + 0{,}2bR_s} \quad (140)$$

Whereas Eq. (139) is linear, Eq. (140) is curved passing through the origin (Fig. 13).

It is evident from Eqs. (138 and 140) that the oxygen consumption rate/unit mass of sludge is a function of Y, b and R_s only. Consequently, if b and Y are correctly determined, then the experimental oxygen consumption rates should serve as a verification of these values. That this is indeed so can be seen from the plots in Fig. 14 of Eq. (140) from Y = 0,43 b = 0,24 and the measured carbonaceous oxygen demand.

If, in conformity to current usage utilizing Eq. (136), i.e. drawing the best straight line through the experimental points in Fig. 14, then a' and b' values are obtained that are unrelated to the Y and b values of Eq. (140). Thus the current method of analysis gives empirical constants for linearized fits of the experimental data unrelated to the basic parameters Y and b. The procedures consequently can be of use only for deriving *ad hoc* parameters for a specified waste over a specified range of R_s, but not of use for research into the basic kinetics of the system.

Marais (1973) proposed a method of analysis which utilizes Eq. (133) directly. The analytical procedure is as follows: Assume Y = 1,0. Select a series of b values (say b = 0,1; 0,15; 0,20, etc.) and for each b value using Eq. (133) calculate SUR_v for a series of R_s values. Plot a log SUR_v versus log R_s curve for each selected b value. (See Fig. 15.) Now plot the experimental SUR_v versus R_s values. Trace the theoretical set of b curves on

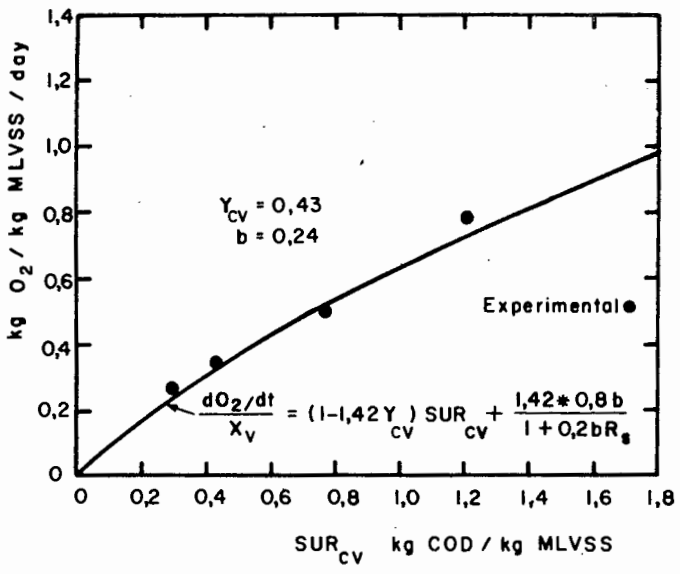

Figure 14
Experimental and theoretical oxygen demand per unit mass of MLVSS versus substrate utilization rate

transparent paper and displace parallel to the SUR axis until a b-curve is over the experimental plots. The b-curve that gives the best fit to the experimental data forms an estimate of b. The value of Y is now determined as follows: From Eq. (133) one can deduce that

$$\frac{SUR_v(Y = 1,b)}{SUR_v\,(exp)} = \frac{Y(exp)}{Y = 1} \qquad (141)$$

i.e.

$$Y\,(exp) = \frac{SUR_v(Y = 1,b)}{SUR_v\,(exp)} \qquad (142)$$

To apply Eq. (142), at some value of R_s draw a horizontal line to intersect the SUR_v(exp) and SUR_v(Y = 1,b) curves at Points A and B respectively then Y(exp) = B/A (Fig. 15).

The value of Y and b obtained by the procedure above is now checked as follows: Inserting the Y and b values in Eq. (140) a

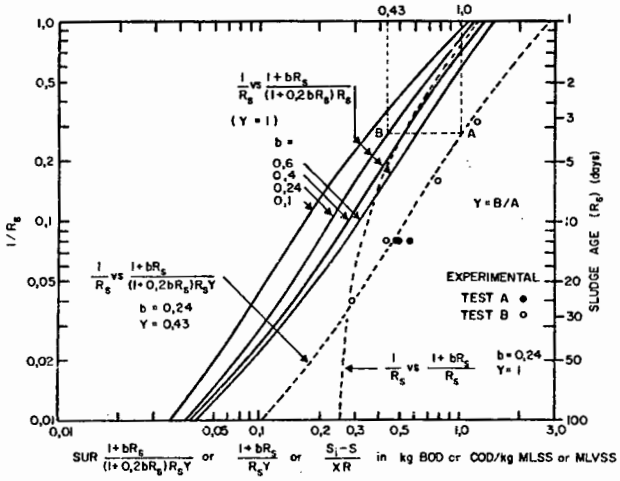

Figure 15
Modified procedure to determine Y and b from experimental data

plot is made of MO/MX_v versus SUR_v. The experimental values are also plotted and these should be near, or, straddle the theoretical curve.

Marais' method leads to consistency between the net sludge generated and the oxygen utilized. In this respect it constitutes an advance on the methods currently being used. However, in Fig. 15 it can be noted that the curvature and shape between two adjacent b-curves are not very different and it is usually impossible to identify positively which b value should be selected. Each time a b value is selected a corresponding Y value is determined. Within limits all the sets of Y and b give virtually identical values for MX_v and MO/MX_v, between R_s = 3 and R_s = 30 days. This is illustrated in Table 3 and in Fig. 16 for the two sets Y = 0,43; b = 0,24 and Y = 0,32; b = 0,1. It is clear that Marais' method gives rise to consistent kinetic interrelationships but not necessarily the correct parametric values for Y and b.

After many endeavours to obtain a more positive identification of Y and b it was concluded that the compensatory effects of Y and b made it unlikely that good identification could be achieved by a joint analysis. The only solution appeared to be an additional *independent* determination of either Y or b. Such a determination for the value of b, is available in the theory on sludge digestion.

In the section on aerobic sludge digestion, two methods were proposed to determine b, by (1) measuring the change in vol-

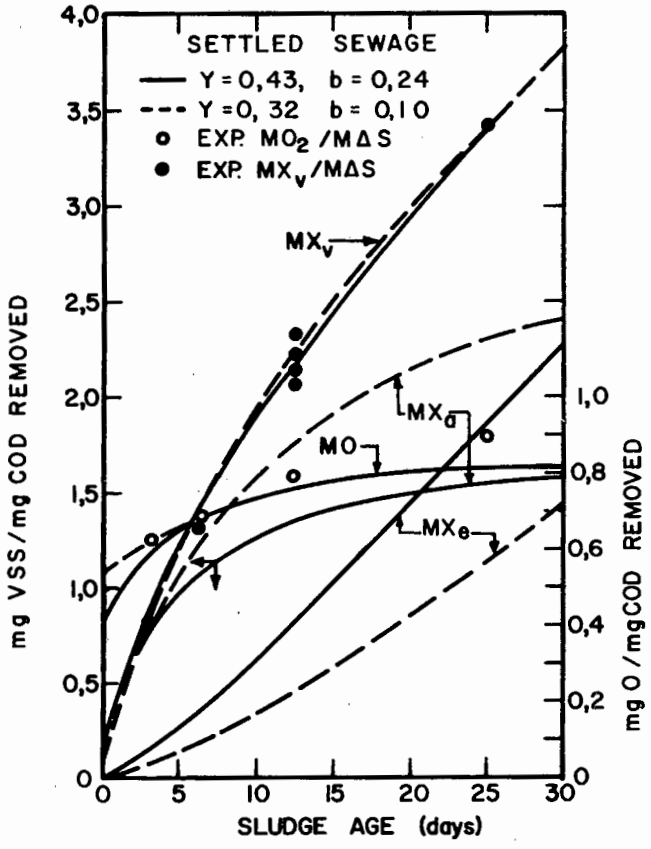

Figure 16
Experimental and theoretical relationships between mass of sludge production and oxygen requirements per day for one mg COD utilized per day in activated sludge process

TABLE 3

THEORETICAL MASSES OF VOLATILE SOLIDS AND OXYGEN DEMAND IN REACTOR PER MASS OF COD UTILIZED/DAY FOR TWO VALUES OF Y AND B

	Y = 0,43, b = 0,24				Y = 0,32, b = 0,01			
R_s	MX_a	MX_e	MX_v	MO	MX_a	MX_e	MX_v	MO
1	0,346	0,017	0,363	0,484	0,291	0,005	0,297	0,579
2	0,581	0,028	0,609	0,567	0,533	0,021	0,555	0,606
3	0,750	0,108	0,858	0,594	0,738	0,044	0,783	0,629
5	0,977	0,235	1,212	0,655	1,067	0,107	1,173	0,666
10	1,265	0,607	1,872	0,734	1,600	0,320	1,920	0,727
15	1,433	1,032	2,465	0,767	1,920	0,576	2,496	0,763
20	1,483	1,423	2,906	0,794	2,133	0,853	2,986	0,788
25	1,536	1,842	3,379	0,808	2,286	1,143	3,429	0,805
30	1,573	2,265	3,838	0,879	2,400	1,440	3,840	0,818

R_s = sludge age in days
MX_a
MX_e = kg active, endogenous and total volatile solids in reactor/kg mass of COD utilized/day
MX_v
MO = kg oxygen utilized/kg COD utilized/day
Y = kg VASS synthesized/kg COD utilized
b = Δmg VASS/mg VASS/day

atile solids and applying Eq. (67) and (2) measuring the oxygen utilization rates and applying Eq. (72). After completing a number of b determinations using both methods it was concluded that the two methods give approximately the same value for b but that method (2) was less laborious and gave more consistent results.

In method (2), to determine b a series of activated sludge plants are run at the desired temperature, at sludge ages ranging from 2,5 days to 30 days. The plants are run until all show steady state behaviour with respect to volatile solids and oxygen utilization rate. The feed to each plant is then terminated and the oxygen utilization rate measured by means of an oxygen probe four to ten times per day for about two weeks. The values are plotted log (dO/dt) versus t and the best straight line drawn through the plotted points. The slope of the plot gives an estimate of b. An example of such a plot is shown in Fig. 17.

From a number of such tests, at different sludge ages, but at the same temperature, it was concluded that b was constant and independent of R_s, with the value b = 0,24/d at 20°C Fig. 18). Repeating the set of tests at 14° and 10°C. showed that b was not very temperature sensitive and its value related to temperature by

$$b_T = 0{,}24(1{,}029)^{T-20} \qquad (143)$$

where

B_T = b(day^{-1}) at T°C
T = °C

The experimental temperature data are shown plotted in Fig. 19.

Once the value of b was found, then using the method of Marais, the associated value of Y was determined, to give Y = 0,43 mg VSS/mg COD removed per day at 20°C (Fig. 14). Data from tests other than 20°C gave Y values apparently not significantly different from Y = 0,43, but the number of tests was too small to come to a firm conclusion as to the effect of temperature on Y. However, it would seem that the temperature effect on Y is very small.

A search of the literature provided some experimental data by means of which it was possible to obtain checks on the val-

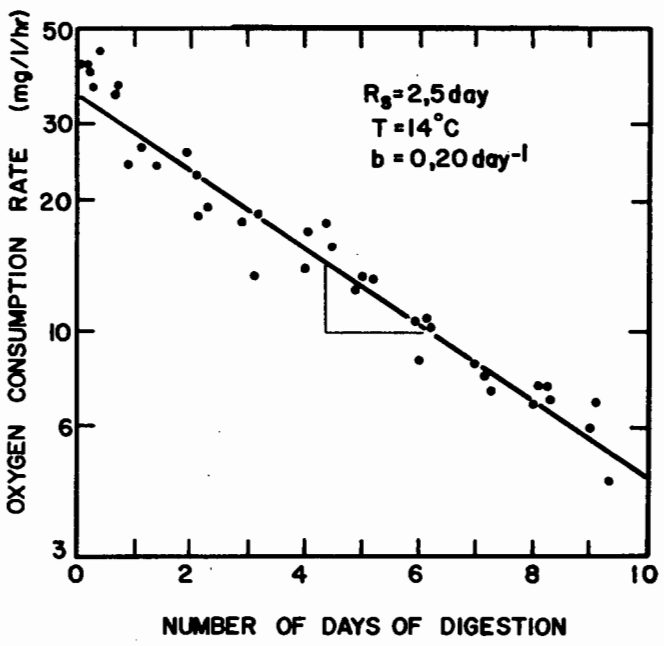

Figure 17
Experimental relationship between oxygen consumption rate with time in a batch digestion test, to determine the endogenous respiration rate, b

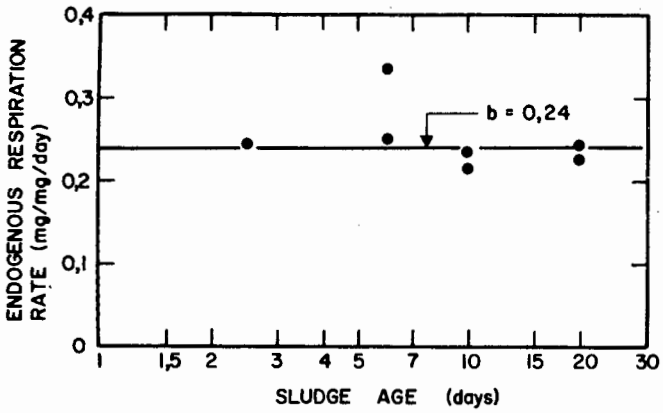

Figure 18
Constancy of the endogenous respiration rate, b, with sludge age

ues of Y and b obtained in this investigation. Most research work in the past utilized the 5 day BOD and Total Settleable Solids, X_T, as the energy and solids parameters respectively. However, one can convert to these parameters from the parameters in the investigation (COD, X_v) by utilizing the relationships observed between COD and BOD_5, and X_v and X_T on plants treating municipal sewages. The relationships expressed in terms of BOD_5, X_v and X_T are given in Eqs. (177) and (178).

Hopwood and Downing (1965) and Wuhrmann (1964) provide plots of $SUR_{BOD,T}$ versus R_s shown in Figs. 20 (a and b). The theoretical plots utilizing Eq. (178) for $Y_{BOD,T}$ = 1,09 and b = 0,2 are also shown. The $Y_{BOD,T}$ and b values are derived from the work in this investigation and are independent of the data of Hopwood and Wuhrmann. The value of b is that of 14°C, Eq. (143). This lower value was selected as being more representative of conditions in England and the European continent.

Considering that the value of $Y_{BOD,T}$ was derived quite independently of the experimental data in Figs. 20 (a and b), from data in this investigation, the fit is quite remarkable.

Determination of K

Theoretically the reaction rate constant K can be determined using Eq. (31), written in the following form

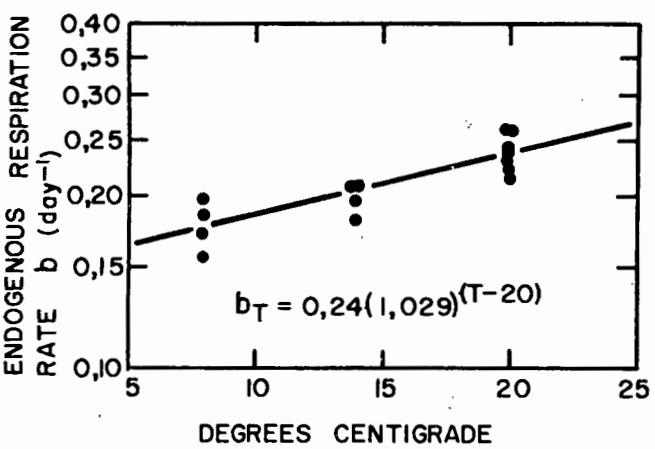

Figure 19
Variation of endogenous respiration rate with temperature

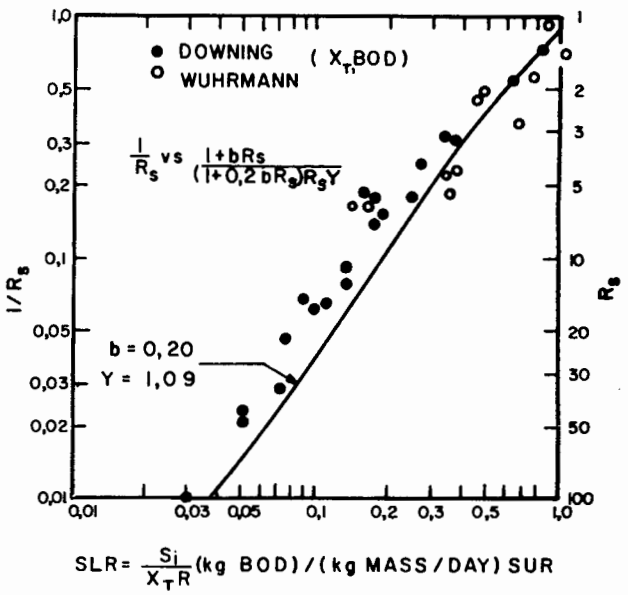

Figure 20(a)
Experimental and theoretical relationship between sludge loading rate and sludge age for two plants in Europe

$$\frac{S_i - S}{X_a R} = SUR_a = KS \qquad (144)$$

where

K is ℓ/mg mass of active material/d.

A plot of SUR_a versus S should be a straight line passing through the origin, the slope defining K.

In practice it is not possible to use Eq. (144) directly as X_a cannot be measured. Consequently the practice has been to substitute X_v for X_a, i.e. a plots mode of

$$\frac{S_i - S}{X_v R} = SUR_v = KS \qquad (145)$$

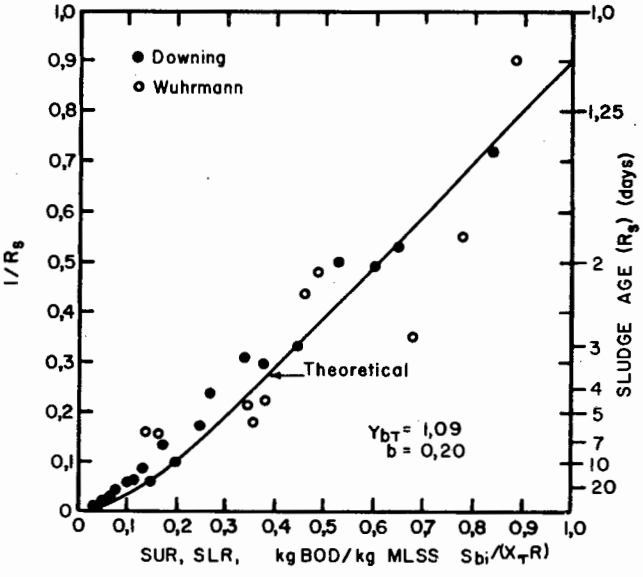

Figure 20(b)
Cartesian plot of SLR versus $1/R_s$ for data from two plants in Europe showing curvature to the origin

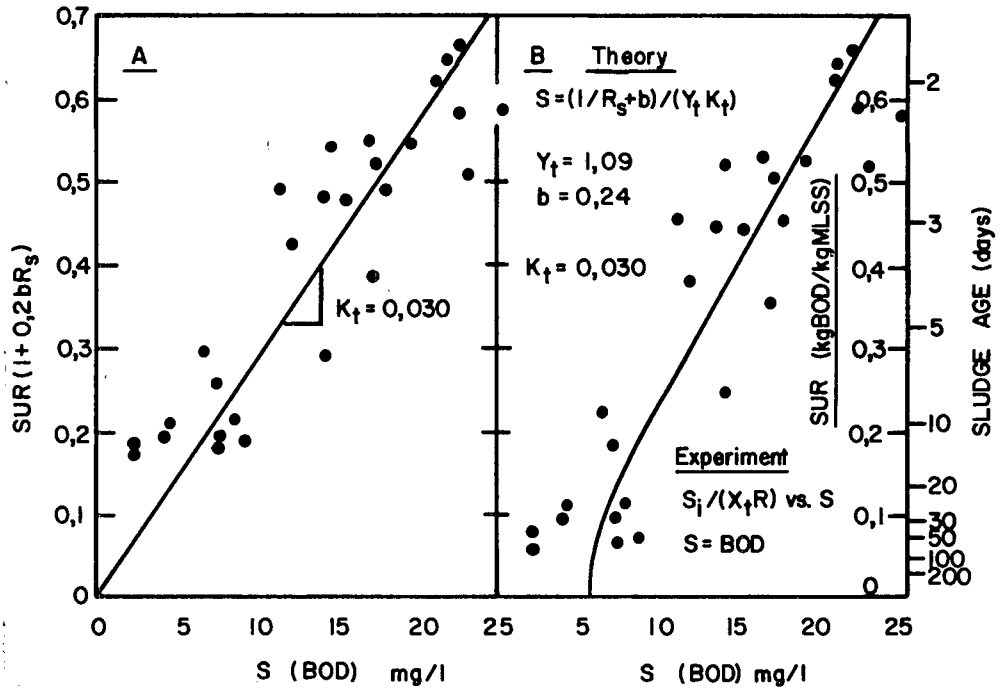

Figure 21

Determination of K for energy measured as BOD. Comparison of new method of plotting (LHS) with standard method of plotting (RHS)

However, it is a simple matter to convert Eq. (145) to the correct form:

$$X_v = X_a(1 + 0{,}2bR_s) \tag{146}$$

Hence

$$\frac{S_i - S}{X_aR} = \frac{S_i - S}{X_vR} \cdot (1 + 0{,}2bR_s) = KS \tag{147}$$

Hence to obtain the correct value of K the measured SUR_v values are multiplied by $(1 + 0{,}2bR_s)$ before making the SUR versus S plot. For practical purposes the value of b can be estimated, from Eq. (143).

The error incurred by not making the correction to SUR can be shown to be as follows: In Eqs. (144 and 145) substitute SUR_{aT} and SUR_T respectively, i.e.

$$\frac{1 + bR_s}{Y_TR_s} = K_TS \tag{148}$$

$$\frac{1 + bR_s}{Y_TR_s\,(1 + 0{,}2bR_s)} = K_TS \tag{149}$$

In Fig. 21 are shown plots of Eqs. (148 and 149) for Y = 1,09; b = 0,24; K_T = 0,03. The SUR_T plot is curved, intersection the S axis, whereas the SUR_{aT} plot is a straight line. Hence, if the best straight line is drawn through the SUR_T data it will probably show an intercept on the S axis. A search of the literature does indeed indicate that often an intercept on the S axis is observed (von der Emde, 1972; Garret, 1972). The data plotted in Fig. 21 is from Garret (1972). In the literature the reason advanced for this behaviour is that there is an unbiodegradable BOD present, but this argument does not appear to be valid as the nature of the BOD test is such that it can only measure biodegradable material.

When the COD is employed as energy parameter the data always shows an intersection on the S axis, but this is due to an unbiodegradable component in the measured COD. The unbiodegradable S value is estimated from the intersection on the S axis. A plot of effluent soluble COD values versus the *corrected* SUR values is shown in Fig. 22 for wastewater from Cape Town, giving a K value of 0,07 ℓ/mg/d.

When searching for K values in the literature the following should be noted:

1. In analyses of the experimental data the determination of K is not significantly affected by using the SUR_v instead of the SUR_a parameter.

Generally the determination is affected significantly only if R_s is very long, i.e. >15 days.

2. The value of K is not affected by using BOD or COD as energy parameter. This can be shown to be so by using Eq. (132) written as follows:

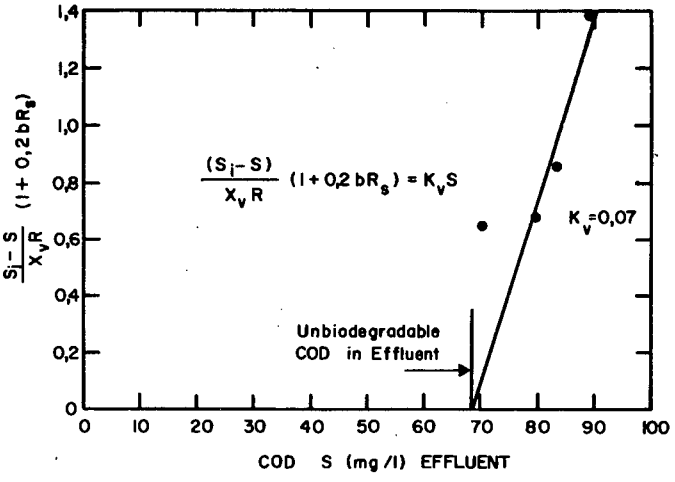

Figure 22

Determination of K for energy measured as COD.

$$\frac{1}{R_s} = Y_{COD}K_{COD}S_{COD} - b \quad (150)$$

$$\text{Now } \Delta S_{COD} \approx 1{,}9\ \Delta S_{BOD} \quad (151)$$

and as the same mass of organisms is synthesized from a substrate, independent of the parameter for measuring the substrate

$$Y_{COD}\Delta S_{COD} = Y_{BOD}\ \Delta S_{BOD} \quad (152)$$

Substituting Eq. (151)

$$Y_{BOD} = 1{,}9\ Y_{COD} \quad (153)$$

$$\text{As } \Delta S_{BOD} \approx \Delta S_{COD}/1{,}9 \quad (154)$$

hence

$$\frac{1}{R_s} = Y_{BOD}K_{BOD}S_{BOD} = (1{,}9\ Y_{COD})K_{BOD}(S_{COD}/1{,}9)$$
$$= Y_{COD}K_{BOD}S_{COD}$$

As b is common in all the equations

$$K_{BOD} = K_{COD} \quad (155)$$

3. The value of K changes if TSS (K_T) is used instead of VSS (K_v), i.e. $K_T \neq K_v$.

In Eq. (30) S is common, i.e.

$$S = \frac{1 + bR_s}{Y_vK_v} = \frac{1 + bR_s}{Y_TK_T} \quad (156)$$

i.e.

$$\frac{K_v}{K_T} = \frac{Y_T}{Y_v} \quad (157)$$

i.e.

$$K_T = K_v \cdot \frac{Y_v}{Y_T} \quad (158)$$

Y_v/Y_T is approximately equal to 0,75

i.e.

$$K_T \approx 0{,}75\ K_v \quad (159)$$

Many values of K_T have been reported in the literature. According to von der Emde (1972) the greater the fraction of industrial waste in the municipal waste flow, the lower the value of K_T. This is supported by the values of K_T listed by Eckenfelder (1967). He gives a range of K_T values for municipal wastes from 0,017 to 0,043. The value for Manchester, a heavily industrialised city, is $K_T = 0{,}017$, which is near the lower end of the range. Data from laboratory scale activated sludge units treating settled sewage from the Athlone works at Cape Town give $K_v = 0{,}07$, i.e. $K_T = 0{,}052$, which is a high value. In general it is difficult to predict what the value of K will be for a plant. For design, one would tend to use a high value when calculating oxygen requirements, and a low value when calculating effluent qualities.

The experimental determination of K is in essence unsatisfactory. The effluent must be centrifuged or filtered to determine S, and in this way some unbiodegraded biodegradable particulate influent material is removed and not reflected in the S value. This deficiency probably has a more severe effect than

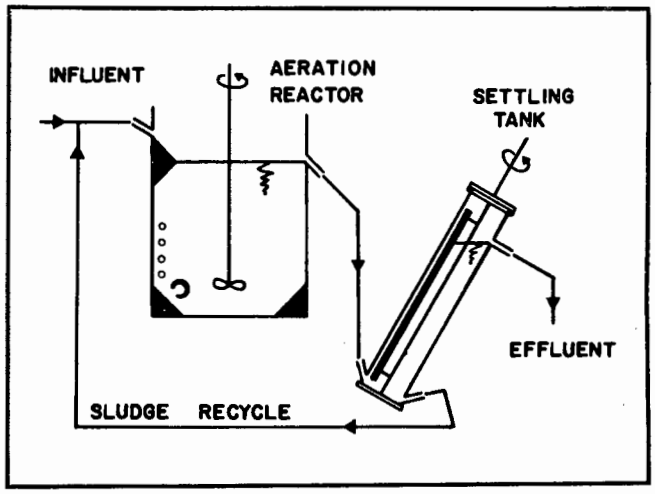

Figure 23
The laboratory scale single tank activated sludge process used in the investigation

is realized as up to 70 percent of the influent COD of municipal wastewater may be in a finely divided suspended particulate form.

Apparatus and methods

Investigation into the kinetics of the activated sludge process is time consuming and tedious. To obtain consistent and reliable data the experimental apparatus must be of appropriate design and there must be an uncompromising vigilance, a strict discipline and attention to detail in every operational procedure and test. If these are relaxed or neglected, the investigation is best left alone – the results will be largely useless.

The experimental phase forms such a pivotal part in an investigation that it is profitable to review the apparatus and operational procedures which, in the authors' experience, have shown to give rise to good experimental data.

A schematic design of a laboratory scale completely mixed activated sludge unit is shown in Fig. 23*. In detail, the plant consists of:

1. *Main aeration reactor.* It is an open container, rectangular in plan, of 10 to 20ℓ capacity. It has an overflow at one end which can be of one or two types: (a) a direct overflow at surface level. The overflow is protected from wave action by a semi-circular section about 40 mm deep set about 20 mm into the liquid. If this is not provided, the outlet periodically blocks from adhering growths (due to splashing) becoming attached above the water level. The outlet pipe is set to slope at 10° down and the plastic connecting tube is nicked to allow bubbles trapped in the inlet to escape, otherwise the bubbles pass down the tube. This outlet has the disadvantage that it is fixed so that the volume of the reactor can only be changed by taping plastic sheets on to the inside walls of the tank to block off a smaller compartment. Here very good long lasting results are obtained using "Elastoplast" water repellent surgical tape. Indeed, it is possible to construct the reactor using this tape only, for tem-

***Detailed design drawings are available of all the apparatus described in this section.**

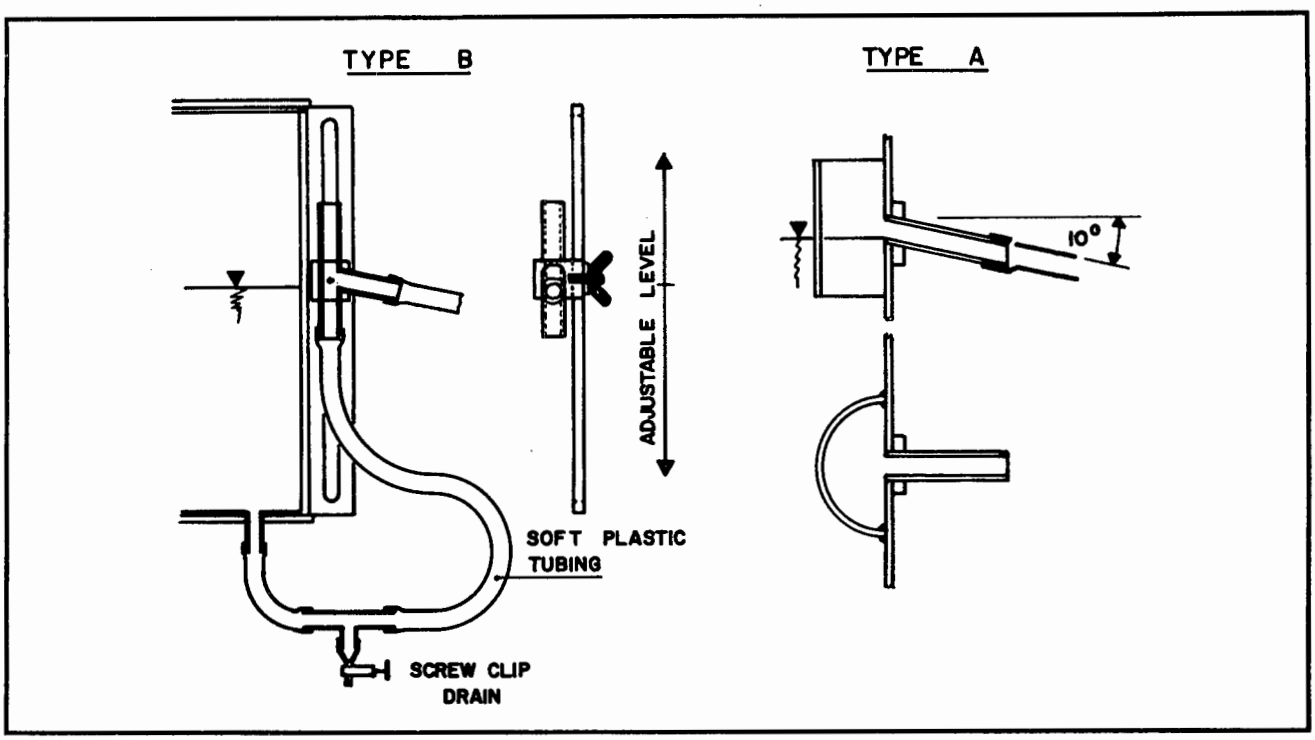

Figure 24
Design details of activated sludge laboratory scale unit

porary purposes (Fig. 24). (b) The liquid leaves the reactor at the botton via a soft plastic tube to the outlet which is a manufactured inverted Y piece that can be set at any level by bolting to a slide fixed to the reactor side. This outlet allows the volume of the reactor to be changed as desired, but trouble is sometimes experienced with the plastic tube becoming blocked under low flows, (Fig. 24).

2. *Paddle stirrer.* This is a separate unit. The paddle is set at the end of a shaft driven by an electric motor, at about 100 rpm. The motor is fixed to a platform which rests on the top edge of the reactor. The paddle-motor assembly can be removed by lifting off the whole assembly. The size of the paddle is found by trial and error. The objective of the stirrer is to keep the contents mixed independent of the aeration mixing effect. Mixing must be independent of aeration in order to control the oxygen concentration to any level desired, and in order to do oxygen utilization tests (see later). The intensity of the paddle mixing must be regulated to a gentle mix sufficient to keep the sludge in suspension throughout the reactor, but insufficient to promote appreciable oxygenation.

3. *Rough bubble aerator.* This is simply a vertical 3 to 6 mm glass tube held vertically in position by clips either to the sides or on to a narrow platform fixed across the top of the aeration chamber. Fine bubble aeration, through a fritter or porous plate is not recommended. The fine bubbles, on bursting at the surface, splatter sludge particles over the plant and this constitutes an unknown loss of sludge. The air supply to the aerators is usually reduced, i.e. ± 10 kPa, by passing through a reducing valve. The low pressure supply is washed by passing through a large washing bottle. The supply of air must be adequate and transported in relatively large pipes so that if more than one aerator is being fed from the low pressure manifold the supply pressure to one aerator is not affected by changing the flow to another aerator.

4. *Settling tank.* This is of the inclined tube type having a central motor driven shaft to which is attached a windscreen wiper to sweep the inside clean, rotating at 1 rpm. Mixed liquor is introduced at the bottom and withdrawn at the bottom, the overflow discharging at the top. At recycle rate of about 1:1, the accumulation of sludge at the bottom is negligible and the sludge always remains aerobic. This settler is the only one of the types tested that has given continuous trouble-free efficient performance.

5. *Daily feed container.* The container is made of 450 or 600 mm diameter plastic pipe with a flat bottom plastic welded to it. The feed take-off is about 15 mm above the bottom. The contents are gently stirred by a motor-driven paddle to keep the solids in suspension at about 20 rpm. The paddle size is found by trial and error. To prevent oxygen entering the feed liquid the paddle shaft passes through a floating cover of plastic-lined expanded styrine. The motor driving the paddle is fixed to a platform that fits on the container top edge. To prevent the paddle fouling the floating cover when the feed level drops to near the bottom, lugs are welded to the inside of the container wall at a level just higher than the top edge of the paddle to give clearance to the paddle.

6. *Peristaltic feed and recycle pump.* The cirular type of peristaltic pump was the only one used in this investigation. It has rollers that can be adjusted to different types of feed tubing. In all cases the speed of the pump should be controlled by either an infinite gear change capability, or electronically. Pumps which

have only finite gear speed changes with a constant motor drive are not recommended as it is not possible to make minor adjustments to the flow. Such adjustments are often necessary as the volume of the feed tubes in the pump tend to change with use, becoming more oval in shape. Also if a stoppage has occurred, it is necessary to increase the feed rate for a period.

If the recycle flow and feed flow are approximately the same, one pump only is required to drive both flows. Preferably two separate pumps should be supplied to control the feed and recycle independently.

7. *Connecting tubing*. These must be of soft, transparent plastic 10 to 15 mm diameter. It is important to have soft tubing so that the tubes can be cleared internally of attached sludge by squashing. The diameter of the tubing may be important; if too small the free flow from the reactor to settler may be inadequate, if too large settlement tends to occur in the tube.

In investigations where serial reactor flow régimes are required, for example, in biological nitrification-denitrification studies, or when simulating plug flow systems, the reactors may range in number from 2 to 6. Of necessity each of the reactors will be smaller in volume. Some reactors can then be made of 150 to 300 mm acrylic transparent pipe. To prevent rotation of the liquid and to promote mixing, vertical vanes are glued to the inside of the reactor. Each reactor has its own mixer and air supply.

The units are mounted on a vertical board, each unit either being bolted directly to the board, or placed on a support bolted to the board. The board is held in a vertical metal frame which itself is mounted on a horizontal frame on roller wheels so that the frame, plus units, can be moved to any convenient place in the laboratory. Below the units, on the ground, is placed a wide shallow sheet metal container to catch and retain any sludge spillage due to blockages and splitting of the tubes. The spilled sludge is returned to the system. It is essential to have the shallow sludge spillage container: at long sludge ages any unaccounted sludge loss will only be made good both in constitution and mass after about one sludge age has passed.

The influent supply, whether settled or raw sewage, is collected in a 400 ℓ trailer tanker. The contents are pumped to two 200 ℓ stainless steel storage vessels in a cold room, kept at 4°C. While pumping to the storage vessels the contents of the tanker are violently agitated by a strong jet of compressed air. The flow passes through a special fine macerator before entering the storage vessel, to cut up, very finely, any solids in the supply.

The tanker supply is delivered two or three days before the previous supply is exhausted. A day before the supply is to be used, ten samples of the storage vessel are analyzed for COD and TKN. Before any sample, or the daily feed, is taken from the storage vessel, the liquid contents must be thoroughly mixed. A simple, effective mixer is a wooden disk 300 mm in diameter fixed through the centre, at right angles, to the end of a wooden rod. Mixing is done by vigorously raising and lowering the disk in the tank contents. Continuous mixing by motor-driven paddles is not desirable as this leads to aeration of the supply. Intermittent mechanical mixing, when collecting the supply, is not worth the complexity and cost.

During the first two days the COD in the storage vessel tends to decrease slightly. Thereafter, the concentration stabilizes. There is little one can do about this and it must be accepted that the influent feed to the reactors is not quite the same in constitution as that in the sewer. It is the price to be paid in order to have a stable feed for a period.

The COD of the daily feed to the units is fixed by estimating the lowest COD to be expected in the waste supply. Consequently the COD in the storage vessel is normally higher than that specified for the feed. Therefore, the daily feed supply must be diluted to the right concentration. Every two days the storage vessel contents are tested for the COD and the dilution changed appropriately to keep the feed COD concentration constant.

Occasionally, under normal conditions, and quite often during the rainy season, the COD in the supply is lower than that specified in the feed. To cope with these exceptions, the volume of the daily feed must be increased so that the same mass of COD is fed (or utilized) every day, i.e. for any steady state work the daily mass of COD fed must be kept constant, irrespective of the strength of the feed.

To obtain as precise control as possible on the COD mass fed per day, the volume of feed each day is measured off and the feed mechanism set to deliver this volume in 23½ to 24 hours. If the feed mechanism breaks down during the night, then during the next day the feed rate must be stepped up to deliver the backlog volume plus the current days volume. Daily feeding should commence about 4 p.m. and sampling and testing of the system at about 10 a.m. to minimize the effect of the slight break in feeding every day at 4 p.m.

The objective of all these control procedures is to ensure that over a period of time stable conditions can develop. It is not so vital that the mass COD fed on two succeeding days have differed (due to a breakdown), but it is essential that over a period of say a week the same mass of COD has been fed as over the previous week, if stability in the sludge concentration is to be attained.

The sludge age is established by "hydraulic control". If, for example, a sludge age of 10 days is wanted and the volume of the reactor is 15 ℓ, then each day 15/10ℓ = 1,5 ℓ of mixed liquor is abstracted directly from the reactor and wasted. No attempt is made to control the sludge concentration. Under the constant feed and hydraulic control of the sludge age, the sludge concentration finds its own level and this is utilized in determining the kinetics of the system.

Sludge draw-off is done once a day for sludge ages of 15 days or more. For sludge ages between 8 and 15 days, sludge draw-off is twice a day, half in the morning and half at night. At sludge ages of less than 8 days the sludge draw-off should be semi-continuous, at regular intervals by means of a peristaltic pump. Every hour a timer activates the pump for a few minutes and a fixed volume is pumped from the reactor. It is almost impossible to get the pump to deliver the exact volume in 24 hours. The pump therefore, is set to deliver slightly less than the required volume and the balance made up out of the reactor each day. If the pump is set to work continuously, the rate of flow is so slow that the mixed liquor settles in the tubes and invariably the concentration pumped out is less than that in the reactor. It is for this reason that the pump is set to operate for short periods at high velocity.

Oxygen level in the reactor is monitored by means of an oxygen probe, the level being controlled to between 1,5 and 2,5 mg/ℓ. To maintain the level between these two limits requires regular inspection of the oxygen level over the day. The control is simplified if the flow to each aerator is metered through a flow meter. A record of the air flow rate is often useful in detecting changes in the process.

Two important operational control procedures are: (1) wash the feed container every day, and (2) at least twice a day brush the reactor surfaces thoroughly to dislodge any adhering bacterial growths. At the same time the connecting tubes are squashed, for the same reason. Every week the tubes must be cleaned by flushing with hot water and passing a rod through them. If these precautions are not strictly observed, then continual trouble must be expected from filamentous organisms invading the plant from growth points on the reactor surfaces and tubes.

Sampling and testing should be done at least every second day. The following tests are necessary.

Influent: COD, TKN, and pH, all on unfiltered samples.
Reactor contents:

(a) X_v, X_T, pH SVI and oxygen utilization rates.
(b) COD, TKN, NO_2, NO_3 on filtered samples.
(c) TKN and COD of the filtered sludge.

In (c) the COD measurement may be omitted unless COD/VSS ratios are being investigated. Furthermore, the TKN of the sludge is usually 0,09 to 0,11 with respect to VSS and may be omitted if a slight error in the nitrogen balance is allowable.

Influent samples contain volatile solid material so that the influent COD and TKN must be done by manual methods. For comparative purposes it is therefore advisable also to do manually the COD and TKN on the filtered reactor samples. NO_2 and NO_3 measurements are conveniently done on an auto analyser. SVI tests should include the time settlement curves which are more revealing than the SVI value as to the characteristics of the sludge.

Oxygen utilization rate determinations demand special mention. A test is done *in the reactor*. The oxygen probe is kept in the reactor and the oxygen level increased to 5 to 6 mg/ℓ by extra sparging of air, or additional sparging with pure oxygen. The air flow is then stopped completely, *but the waste feed is continued*, also the mechanical mixer is kept stirring. The change in oxygen concentration is then recorded with time (preferably automatically) and if the data plots to a straight line the rate is determined from the slope. If a sample is taken from the reactor and a rate determination done on it, then often, though not always, the rate can be lower by about 30 percent. This is due to the rapid change in oxygen utilization of a sample once the feed stops, particularly where nitrification is taking place. The gentle turbulence from the stirrer has a negligible effect on reoxygenation and on the rate measured. Let the rate measured be designated by, r mg/ℓ/d, then the oxygen utilization per day is given by:

$$MO_t = rV \text{ mg/d} \qquad (160)$$

Analysis of kinetic response

When making a comprehensive investigation into the response of the completely mixed activated sludge process, two separate sets of investigations are required. The first utilizes settled waste and the second unsettled waste. For the settled waste the inert volatile settleable solids, X_{ti}, are assumed negligible and the constants are determined based on this assumption. For the unsettled waste the above assumption may not hold, but once Y and b are known X_{ti} can be estimated by trial and error to obtain the observed response using unsettled sewage.

Analysis using settled waste

The following information would have been collected:

(1) Influent: COD (S_i), TKN (mg/ℓ) and Q (ℓ/d)
(2) Process constants: V(ℓ), hence R = V/Q (day)
(3) Soluble fraction of reactor contents: COD (S), TKN, NO_3, NO_2, (mg/ℓ)
(4) Volatile solid fraction: MLVSS (X_v), TKN of X_v (optional) (mg/ℓ)
(5) Oxygen utilization: O_t mg/ℓ/d
(6) Endogenous respiration test: b (day^{-1})

With regard to (6) above, if the objective is to obtain design data it is allowable to omit the determination of b and accept the value of b from Eq. (143). For research purposes, b should be determined experimentally.

The following steps in analysis are now taken:

(1) Form $\frac{(S_i - S)}{X_v R} = \frac{(S_i - S)Q}{X_v V} = \frac{M\Delta S}{MX_v} = SUR_v$

from the average value of each test.

(2) Plot SUR_v versus R_s, as in Fig. 15. Plot the theoretical b curve assuming Y = 1, Eq. (133), using the b value obtained earlier. By moving the b curve parallel to the SUR_v axis fit the b curve to the experimental plot, and determine Y, (Eq. 142).

(3) Determine the experimental carbonaceous oxygen demand rate, r_c:

$$r_c = r - 4{,}6\ NO_3 - 1{,}9\ NO_2 \qquad (161)$$

or, from Eq. (160):

$$MO_c = r_c V \qquad (162)$$

Determine from experimental data

$$MX_v = X_v V$$

$$MO_c = r_v V$$

$$M\Delta S = (S_i - S)Q$$

(4) Calculate and plot the following theoretical curves using experimentally determined Y and b values, from Eqs. (56c and 58b):

$$\frac{MX_v}{M\Delta S} = Y\frac{(1 + 0{,}2bR_s)}{1 + bR_s}R_s \qquad (163)$$

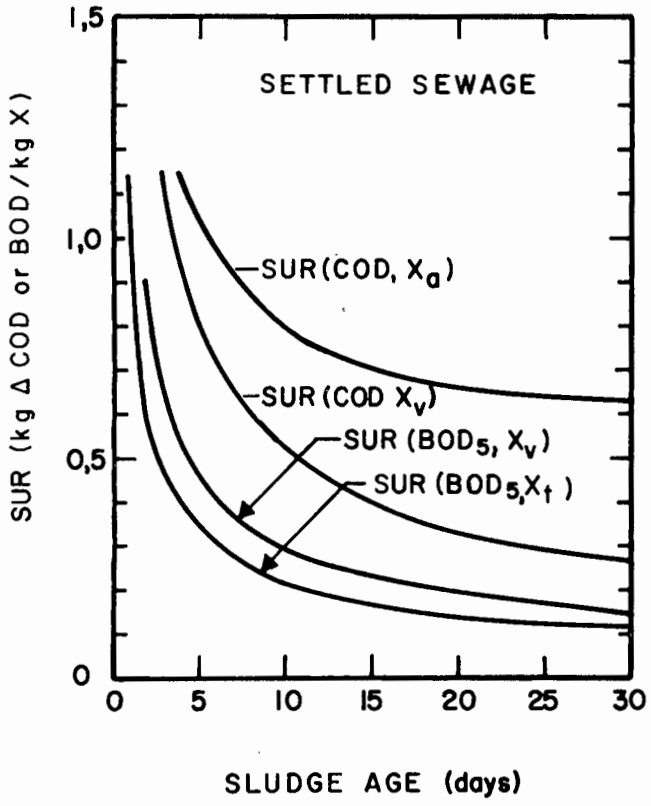

Figure 25
Comparison between various substrate utilization rates and the sludge age

$$\frac{MO}{M\Delta S} = (1 - 1{,}42Y) + \frac{0{,}8.1{,}42bYR_s}{1 + bR_s} \quad (164)$$

(5) Plot the experimental $MX_v/M\Delta S$, $MO/M\Delta S$ values on the same diagram as in (4) above. The data should plot around the theoretical lines. If not, make slight changes in Y and replot the theoretical lines until the best fits are obtained (see Fig. 16).

(6) Once b is known, plot from Eq. (147)

$$(1 + 0{,}2bR_s)\frac{(S_i - S)}{X_vR} \text{ versus } S$$

to obtain the value of K_v and the unbiodegradable soluble COD fraction, S_u (see Fig. 22).

Unsettled waste

To determine the unbiodegradable influent volatile solids concentration X_{ii}, the set of tests above is repeated using unsettled wastewater. In the analysis Y and b obtained from the settled waste tests are now assumed to be valid for the unsettled waste. An estimate of X_{ii} is now made as follows:

$$X_{ii} = C_{xii}S_o \quad (165)$$

Where S_o is equal to COD of influent,

C_{xii} = fraction of X_{ii} with respect to S_o

Then

$$S_i = S_o - 1{,}42\ X_{ii} \quad (166)$$

Plot the following theoretical functions versus R_s:

$$\frac{MX_{vt}}{M\Delta S} = \frac{X_{vt}V}{(S_i - S)Q} = \frac{Y.(1 + 0{,}2bR_s).R_s}{1 + bR_s} + C_{xii}S_oR_s \quad (167)$$

for C_{xii} = 0,04; 0,06; 0,08; etc.

Plot the experimental $\frac{X_{vt}V}{(S_i - S)Q}$ versus R_s

and select the best C_{xii} value.

Once C_{xii} is selected the check is made against the oxygen demand rate using the procedure outlined for Eq. (164) above, remembering that $\Delta S = S_i - S$, not $(S_o - S)$.

It is always desirable to check the nitrogen balance. If no nitrogen is lost by dentrification then

$$TKN_{inf}.Q = [TKN_{ef} + (NO_3 - N) + (NO_2 - N)]Q + f.(MX_v)/R_s \quad (168)$$

If f had not been measured a good check is still obtained by taking f = 0,1.

Process Design and Control

Loading rate versus sludge age

In this paper the underlying theme that has emerged is the fundamental importance of the sludge age as a parameter in the kinetics of the activated sludge process. It is now necessary to consider in greater detail its influence on the design and operation of full scale works.

A widely accepted basis for design of full scale plants is the Sludge Loading Rate (SLR), also known as the Load Factor, or, as defined in this investigation, the Substrate Utilization Rate (SUR_v). Now it has been shown earlier that the SUR always can be written in terms of the sludge age (Eq. 133), but as the defining equation also contains the terms Y and S, a number of SUR values can be evaluated depending on the choice of solids measurement (X_a, X_v, X_T) and substrate measurement (COD, BOD). The derivation of some of these SUR parameters are given below and plotted in Fig. 25.

Let $Y = 0{,}43\ M\Delta X_a/M\Delta COD$ (169)

For municipal settled sewage

$$\Delta BOD = 1{,}9\Delta COD \quad (170)$$

and

$$X_v/X_T = 0{,}75 \quad (171)$$

Then from Eqs. (169 and 171):

$$Y_{BOD,v} = 1{,}9Y = 0{,}817\ M\Delta X_a/M\Delta BOD \quad (172)$$

$$Y_{BOD,T} = T_{BOD,v}/0{,}75 = 1{,}09\ M\Delta X_{aT}/M\Delta BOD \quad (173)$$

From Eq. (56d) defining

$$Z = \frac{1 + bR_s}{(1 + 0{,}2bR_s)R_s} \quad (174)$$

$$M\Delta COD/MX_a = SUR_a = (Z/Y)\ (1 + 0{,}2bR_s) \quad (175)$$

$$M\Delta COD/MX_v = SUR_v = Z/Y \quad (176)$$

$$M\Delta BOD/MX_v = SUR_{BOD,v} = Z/Y_{BOD,v} \quad (177)$$

$$M\Delta BOD/MX_T = SUR_{BOD,T} = Z/Y_{BOD,T} \quad (178)$$

$$\frac{MO}{M\Delta S} = 1{,}9[(1 - 1{,}42Y) + \frac{1{,}42.0{,}8bYR_s}{1 + bR_s}]$$

$$= (1{,}9 - 1{,}42Y_{BOD\ v}) + \frac{1{,}42.0{,}8bY_{BOD,v}R_s}{1 + bR_s} \quad (179)$$

$$\frac{MX_T}{M\Delta BOD} = \frac{1{,}09\ (1 + 0{,}2bR_s)}{1 + bR_s} \quad (180)$$

If raw sewage is being treated, Eqs. (175 to 180) must be modified to incorporate the accumulation of inert material X_i in the sludge derived from the inert material in the raw sludge, X_{ii}. As an example, consider Eq. (176); from Eq., (165) we write $X_{ii} = C_{xii}\ (S_o) = C_f(S_i - S)$ as the fraction of inert material in the influent with respect to the mass of COD biodegraded. Then Eq. (176) becomes:

$$SUR_v = 1/(Y/Z + C_fR_s) \quad (181)$$

It should be noted that if volatile inert material is present, yet another set of SUR values can be calculated.

From Fig. 25 and the discussion above, it is clear that depending on the parameters defining the sludge and substrate a multiplicity of SUR values are possible for the same sludge age. This is an undesirable aspect as it provides a permanent source of error and misunderstanding at, and between all levels of technical staff concerned with the process. But perhaps of greater importance is the fact *that as all the different SUR's are functionally related to the sludge age, no additional information can be derived from the SUR's that cannot be derived from the sludge age.*

Although the R_s value, being independent of the nutrient and sludge parameters, it theoretically superior to the SUR, one should, from a practical point of view, ask this question – "Will the use of parameter SUR or that of R_s lead to better and simpler control of the process?"

At present the process is controlled by keeping the sludge concentration at some constant value which is established either by design or from experience of the plant behaviour. To determine the load factor extensive testing of the daily influent substrate and flow pattern must be undertaken to determine the mass substrate load conditions. To fix the sludge age a history of sludge abstraction must be kept. This, in itself, requires careful recording because the sludge is abstracted from the underflow of the secondary settling tank and the concentration of the underflow tends to vary with the daily cyclic flow through the plant so that the concentration wasted from the underflow must be tested daily. Thus, neither the sludge age nor the load factor is usually known precisely. Even to keep the sludge concentration constant requires continuous evaluation of the sludge mass wasted from the underflow.

The problem is controllable in large plants where the technical supervision is adequate, but in small plants both the load factor and sludge age are usually unknown. It is a real problem to instruct small plant operators in process control; one may, from necessity, have to resort to instructions of the following kind: "Fill a litre measuring flask with mixed liquor, allow to settle for half an hour and if it settles to a value greater than x ml open the waste underflow valve for y minutes". It therefore appears that the current procedures developed from the concept of the load factor (whether explicitly stated or by implication) lead to relatively complicated procedures to exercise control of the plant process.

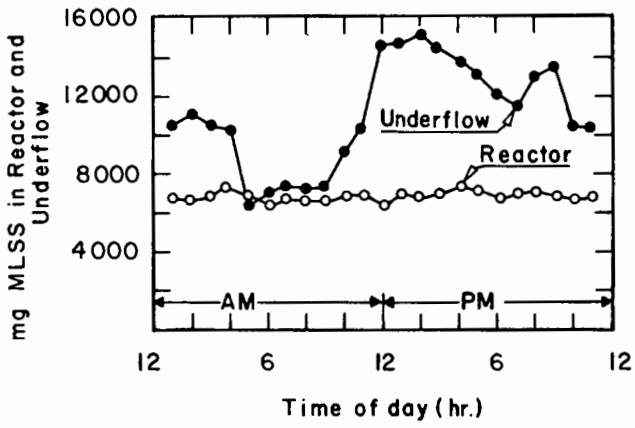

Figure 26
Experimental data from a full scale activated sludge plant illustrating the constancy of the reactor MLSS compared with the settler underflow concentration

Hydraulic control of sludge age

A positive control of the sludge age (and the SLR) can be built into the plant by the method of hydraulic control proposed and implemented by Garret in 1958. The scheme is as follows: Suppose a sludge age of 10 days is specified. A satellite settling tank is provided, completely independent of the secondary settling tank, into which 1/10 of the reactor volume is pumped every day. The supernatant is discharged to the effluent channel (or pumped back to the reactor), the settled sludge is pumped to the digestors or drying beds. (This procedure was already described in the process control of the experimental plants, but bears repeating). That this method gives the correct sludge age can be shown as follows:

$$R_s = \frac{MX}{M\Delta X} = \frac{X_vV}{X_vv} = \frac{V}{v} \quad (182)$$

where

V = volume of reactor
v = volume mixed liquor abstracted per day from reactor.

The procedure works because the mixed liquor concentration changes insignificantly over the day. (Ekama and Marais, 1975). This is verified by comparing the stability of the concentration of mixed liquor in the reactor and the concentration of sludge in the underflow over the day in one of the major plants of Johannesburg, Fig. 26, (Nicholls, 1975).

Controlling the sludge age in small works may require pumping at regular times, every day or every few days, provided the volume pumped is such that the required volume, v, per day is abstracted. In big works the sludge age satellite tank may be designed for continuous operation receiving a constant flow, or, operated for say 12 hours per day.

An important point about hydraulic control of the sludge age is that irrespective of the flow through the plant if a fixed fraction of the volume of the reactor is removed and wasted every

day, the sludge age is fixed. If the COD mass load per day on the plant remains constant, the sludge concentration will remain constant automatically. If the COD mass load increases, the sludge concentration will increase automatically, to maintain the same sludge age. Thus, by monitoring the MLSS concentration an indirect measure is obtained of the COD load and load change.

If the oxygen capacity of the plant becomes insufficient to cope with an increasing load some relief is possible by reducing the sludge age, although the reduction in sludge age must be quite substantial to bring significant relief when the sludge age is long (see Fig. 4).

Using hydraulic control the sludge age is changed by simply changing the volume wasted per day. Furthermore, if say, the sludge age is reduced from 20 days to 15 days by hydraulic control, the full effect of the change will become apparent only after about 10 days. Thus the organisms have an opportunity to adapt gradually to the change in load.

Hydraulic control of the sludge age devolves a greater onus on the designer and removes responsibility from the plant operator. It becomes essential that the designer calculates the sludge mass more exactly, to provide sufficient reactor volume under the design load to give the required concentration of MLSS. Also, the settling tank design, recycle and aeration capacities must be adequate. If these aspects are adequately designed, then with the hydraulic control of the sludge age, plant control is simplified and, on small scale plants, may even do away with the requirements for solids and SVI tests except at long intervals.

Selection of sludge age

Selection of the sludge age for a plant depends on many factors including the quality of effluent required, the stability of the process, whether nitrification is required, whether the waste sludge must be suitable for direct discharge to the drying beds, and so on. Many agencies now demand a nitrified effluent and this requirement puts a lower limit on the sludge age which may or may not fix the minimum sludge age, depending on the temperature. As the nitrification requirement is likely to be a factor of increasing importance in the future, this discussion will be largely limited to the influence of the nitrification requirement on the process design and operation.

In the temperate regions where the water temperatures may fall to values below 10°C, to ensure all year round nitrification the sludge age is unlikely to be less than 10 to 15 days. In contrast, in the tropics and sub-tropics where the water temperature may not fall below 20°C, nitrification can take place at sludge ages of 3 days or less, i.e. *in the tropics it may be impossible to design an activated sludge plant that will not nitrify.*

When nitrification takes place there is always the possibility of denitrification. The unit in the process where this is most likely to occur is in the secondary settling tank.

Many design procedures for the settling tank incorporate a dual function for the tank: (1) for solid liquid separation and (2) for compaction of the sludge. The net mass of sludge to be separated in the settler is QX_v. The mass entering the settler is $(Q + Q_r)X_v$ where Q_r is the settler underflow. The overflow rate, or upward velocity in the settler is not affected by Q_r but depends only on Q (see Fig. 27). At steady state the density of the underflow X_{vr} is

$$X_{vr} = \frac{X_v (Q + Q_r)}{Q_r} = \frac{1 + r}{r}$$

where

$r = Q/Q_r$ and $(1 + r)/r$ is called the densification ratio.

To achieve the necessary densification the sludge mass must build up in the settler to give the required density at the bottom draw-off (see Fig. 27). Hence the sludge is retained in the settler for a period depending on the densification required, the initial concentration, X_v, the geometry of the settler and the settling characteristics of the sludge. All things being equal, if the densification ratio is large (i.e. r is small), the retention time in the settler, to reach the required density, must be long and a considerable accumulation of sludge may occur in the settler. The residence time in the settler promotes denitrification, the degree of denitrification being (1) roughly proportional to the period of residence of the sludge, (2) greater as the sludge age decreases (proportional to the active mass, X_a), and (3) a function of the concentration of stored energy adsorbed onto the organism (Ekama and Marais, 1975; Stern, Wilson, Marsden and Marais, 1976).

If denitrification takes place to a sufficient degree the sludge particles are buoyed to the surface and lost via the overflow of the settler. This phenomenon has been observed: At Bellville, South Africa, the plant loses sludge via the overflow during the latter part of summer, February-March, when the water temperatures are about 20°C. Sludge loss occurs every day towards the afternoon, near the end of the period of high flow and load, when the accumulation of sludge in the settler is at a maximum. Although the recycle is quite high (r = 2 based on mean flow) sufficient sludge still accumulates to make denitrification significant at high temperatures.

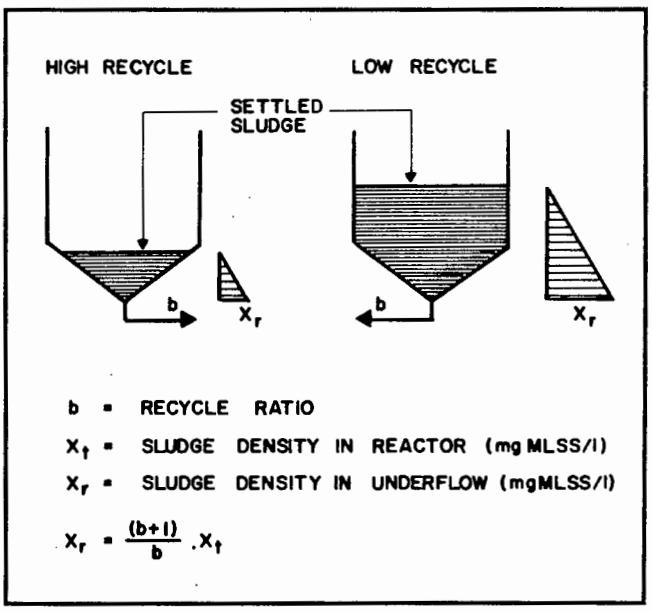

Figure 27
Increased accumulation of sludge in settler with decreased recycle

At Brasilia, the Federal Capital of Brasil, the minimum annual water temperature is 20°C so that nitrification takes place at sludge ages of 3 days and less. The activated sludge plant has a recycle ratio of r = 0,5 maximum and the settler sheds sludge via the overflow all the year round. It has been found impossible to increase the MLSS to a value greater than 1 200 mg/ℓ (which corresponds to a sludge age estimated of 2,6 to 3 days) for then nitrification increases to such a degree that the sludge loss by denitrification is sufficient to reduce the sludge concentration (and sludge age) again to about 1 200 mg/ℓ; in this manner to achieve a state always verging on nitrification. When the sludge concentration was reduced to 1 000 or less ($R_s \approx 2$ days) the problem became less acute, but the effluent quality suffered. At these low sludge ages the sludge consists almost wholly of the active mass fraction, X_a, and theoretically contains an appreciable fraction of adsorbed energy so that denitrification is bound to be prominent. The situation should be alleviated to some degree if the recycle ratio could be increased to say 2, but this is unlikely to eliminate the problem.

The discussion above points to two conclusions:

(1) In a nitrifying plant the settler can no longer serve the dual functions of liquid-solid separation and sludge compaction; the function is changed to that of liquid-solid separation and minimising the holding time of the sludge by using high recycle ratios of say up to 1,5 to 2. The function of thickening must be taken over by a special settler. Once hydraulic control of the sludge age is instituted, the problem of thickening of the wasted sludge in any event passes from the secondary settler to the satellite settler. In the satellite unit liquid-solid separation and thickening by flotation is now both technically and economically feasible (Bratby and Marais, 1976).

(2) It is highly desirable to incorporate into the plant design deliberate biological denitrification using the influent sewage as energy source (Barnard, 1975). The full denitrification process need not be instituted, only the primary anoxic reactor. In the authors' experience with this partial denitrification, the process achieves greater stability, the SVI's are reduced and rising sludge in the settling tank is virtually completely repressed. The denitrification process is considered in detail in the fourth paper of this series.

In the literature the range of SLR values of 0,2 to 0,5 kg BOD applied/day/kg MLSS is often quoted as one in which the settling characteristics of the sludge is optimum. This range of SLR corresponds approximately to a range of sludge ages 10,5 to 2,2 days (Fig. 25). Referring specifically to the treatment of municipal wastewater, the authors' experience is that (1) bad settling sludges may be encountered at any sludge age, due to undetermined causes; (2) the frequency of bad settling increased as the sludge age was reduced below 10 days; (3) the frequency of bad settling increased as the temperature increased – very little trouble with bad settling was experienced at 14°C; (4) bad settling or bulking, due to filamentous growths was always due to fine hair-like blue-green algae of unidentified species, never due to *sphearotilus nutans;* (5) over or under-aeration both induced bad settling sludges; (6) incorporation of a primary anoxic reactor invariably improved the settling characteristics of the sludge, but the time the organisms are under *actual* anoxic conditions must not be too long, about 1 hour maximum; (7) bad settling is often indicated by a reduction in the stalked ciliates and an increase in the free swimming ciliates in the sludge.

Investigating the settleability of sludges derived from municipal wastewaters, Pitman (1974) found that it was poorest at 6 days sludge age and continually improved up to 20 days sludge age. The cause of poor settling was ascribed to the inordinate concentration of free swimming ciliates at 6 days, the concentration decreasing as the sludge age increased. In England, studies at the Water Pollution Research Laboratories (1966, 1967) showed that poor settleability was obtained in the range SLR 0,2 to 0,5 and good settleability outside this range.

It is apparent from this discussion that there are numerous factors, many unknown, that affect the settleability of sludges so that the behavioural patterns observed on one plant may be specific to that plant only.

Complete oxidation

To avoid the complexity in operation arising from anaerobic digestion, there is a tendency at present to design for long sludge ages of 30 days or more so as to achieve a stable sludge suitable for discharge to the drying beds.

In any event when nitrification-dentrification is built into the plant, the sludge ages will be about 10 to 15 days. Once sludge ages of this magnitude are required, it would seem practical to increase the sludge age to 30 days as the oxygen requirement is only about 12 percent more (see below).

There are a number of factors that must be considered when evaluating this problem. Comparing a R_s 15-day plant with a R_s 30-day plant:

(1) The sludge masses in the reactor are

$$\frac{MX_v30}{MX_v15} = \frac{1{,}58}{1}$$

i.e. if the same concentration X_v is used in the two plants, the volume of MX_v30 is about 60 percent greater than MX_v15.

(2) The mass of active material per mass of COD utilized is not very different:

$$\frac{MX_a30}{MX_a15} = \frac{1{,}12}{1}$$

i.e. the rate of reaction does not improve with very long sludge ages; on the contrary the active sludge is simply "diluted" into a bigger mass of inert material.

(3) In nitrification-dentrification plants augmented biological removal of phosphorus by luxury uptake occurs. The phosphorus removed is *inter alia* a function of the sludge age. If the input COD is the same, the mass of P that can be removed increases as R_s decreases down to sludge ages of 10 to 15 days.

However, it seems that the advantages of long sludge ages (i.e. direct discharge to drying beds) can be combined with the advantages of short sludge ages (i.e. enhanced phosphorus removal, and smaller reactor volumes) by adding aerobic digestion to the short sludge age plants. The following example illustrates these points:

Compare the volume of reactor, oxygen demand and sludge constitution of the following three plants: (a) R_s = 15 days, (b) R_s = 30 days, (c) R_s = 15 days plus aerobic digestion to give a sludge of the same quality as from the R_s 30 day plant.

Assume $M\Delta S = 1$, $Y = 0,43$, $b = 0,24$:

R_s30: $MX_a = YR_s/(1 + bR_s)$

$= 0,43.30/(1 + 0,24.30) = 1,57$

$MX_e = 0,2bR_sMX_a = 0,2.0,24.30.1,57$

$= 2,26$

i.e. $MX_v = 1,57 + 2,26 = 3,83$

R_s15: $MX_a = 0,43.15/(1 + 0,25.15) = 1,40$

$MX_e = 0,2.0,24.15,1,40 = 1,01$

$MX_v = 1,40 + 1,01 = 2,41$

These masses are proportional to the volumes if X_v are the same for both plants, i.e.

$V_{30}:V_{15} = 3,83:2,41 = 1,59:1$

Sludge digestion

Active fraction in plant is given by $1(1 + 0,2bR_s)$

R_s30 active fraction $= 1/(1 + 0,2.0,24.30)$
$= 0,41$
R_s15 active fraction $= 0,58$

Digestion required to reduce the R_s15 sludge to the same active fraction as R_s30 is found as follows:

R_s30 mass of sludge wasted/day $= 3,83/30 = 0,126$
i.e. active mass wasted/day $= 0,126.0,41 = 0,052$
R_s15 mass of sludge wasted/day $= 3,41/15 = 0,160$
i.e. active mass wasted per day $= 0,160.0,58 = 0,093$

This means that the active mass from R_s15 must be reduced from 0,093 to 0,052 by aerobic digestion.

Let the digestor be of the single flow through type,
i.e. $R_s = R$, from Eq. (79)
$MX_a = MX_a/(1 + bR)$
$0,052 = 0,093/(1 + 0,24R)$
i.e. $R = 3,29$ days

Check if the inert material discharge by R_s30 and R_s15 plus digestion is the same.

R_s30: $X_i/d = 2,26/30 = 0,0753$

R_s15 digestion $= 1,01/15 + (0,093 - 0,052)0,2$
$= 0,0755$

Hence they are the same.

Oxygen demand

R_s30 MO/d $= (1 - 1,42Y) + 0,8.1,42.bMX_a$
$= 0,389 + 0,8.1,42.0,24.1,57$
$= 0,816$

R_s15 MO/d $= 0,389 + 0,8.1,42.0,24.1,4$
$= 0,770$

Aerobic digestion $= 1,42.0,8.\Delta MX_a\ b.R$
$= 1,42.0,8.0,052.0,24.3,89$
$= 0,046$

Hence for R_s15 + digestion; MO/d $= 0,770 + 0,046 = 0,816$

Comparison of Oxygen Requirements

R_s30	R_s15 + digestion	R_s15
0,816	0,816	0,770
(1,12)	(1,12)	(1)

Comparison of Volumes

R_s30	R_s15 + digestion	R_s15
3,83	2,94	2,41
(1,59)	(1,21)	(1)

Should the influent to the digestor be densified say 10 times, the volume requirements for R_s15 + digestor (densified) equals

$$\frac{(15 + 0,1.3,29)}{15} \times 2,41 = 2,46$$

Comparison of Volumes

R_s30	R_s15 + digestor (densified)	R_s15
3,83	2,46	2,41
(1,59)	(1,02)	(1)

The calculations above are for comparison only. However, they do indicate that considerable reactor volume can be saved by utilizing a 15 day sludge age plus an aerobic digestor with densified sludge, to give a stable sludge of the same character as a plant with 30 days sludge age. Moreover, the digested sludge liquor volume per day is very small, so that the supernatant can be lime treated to precipitate the phosphorus in the sludge from plants in which the activated sludge process is designed for enhanced biological phosphorus removal. It is also possible to design the digestor to remove some of the nitrate (see Appendix A).

Comparison of Design Criteria

The model developed in this paper sets out in detail the procedures for design of the activated sludge process for steady state conditions. It is now of interest to compare the predictions of this theory with other design criteria. Comparison will be limited to the carbonaceous oxygen demand for processes treating settled sewage only.

Vosloo (1970) developed criteria from data obtained by Wurhmann (1964) and Hopwood and Downing (1965). He presented design values for sludge production and oxygen demand in terms of the Sludge Loading Rate and sludge age. The oxygen demand was based on the accepted relationship between the 5-day and ultimate BOD's. Von der Emde (1972) concisely set the design criteria proposed by the ATV Organisation of Germany. Anderson (1973) derived equations for the Sludge Loading Rate, solids production per day and oxygen demand in terms of the sludge age based on the experimental results of Downing. Unfortunately, the source of Downing's results are not listed. With regard to his equation for oxygen demand, this yielded values "lower than those of Downing".

As an example of American practice, the design procedures proposed by Metcalf and Eddy (1972) is selected. The following equations are either given or derived from their work:

$MX_v = Y.M\Delta S.R_s/(1 + bR_s)$
$MO = 1,47\ M\Delta S - 1,42\ MX_v/R_s$
$MX_T = MX_v/0,8$
$\Delta MX_T = MX_T/R_s$

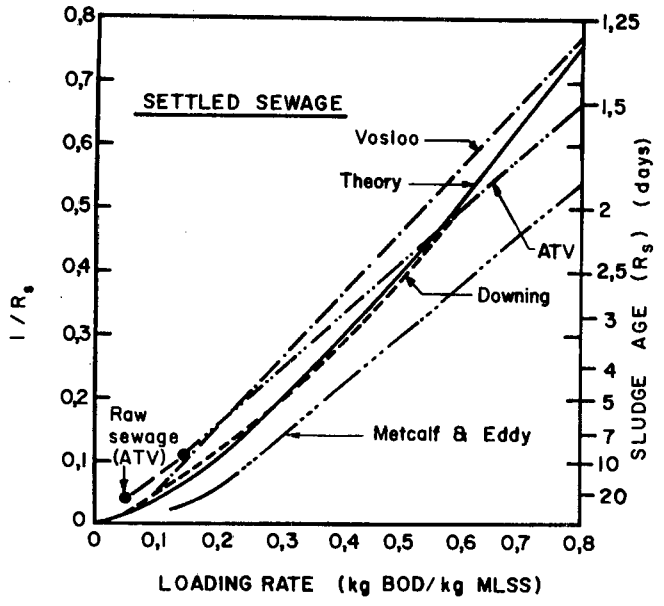

Figure 28
Comparison of relationship between sludge age and sludge loading rate according to different design criteria

where

Y = 0,65 mg VSS/mg BOD_5 removed/day
b = 0,07 mg VSS/mg VSS/d at 20°C.

The following parameters are shown plotted in Figs. 28 and 29 for carbonaceous oxygen demand only.

1. kg BOD_5 load or BOD_5 removed/MLSS versus $1/R_s$ and R_s Fig. 28.
2. kg O/kg BOD_5 load or BOD_5 removed per day versus R_s Fig. 29.
3. kg MLSS produced per day kg BOD_5 load or BOD_5 removed per day versus R_s Fig. 29.

For comparison, plots are also shown of the relevant parameters based on the theory presented in this paper.

The criteria exhibiting similar behaviour are those of Downing-Anderson and the authors. The sludge production per day and the SLR plots are almost identical. The oxygen demand curves are parallel, the Downing-Anderson values being approximately 0,7 of those of the authors'. If one notes that Anderson stated that his oxygen demands are lower than those originally proposed by Downing, it is quite likely that closer correlation could be expected with Downing's original data.

With the exception of the oxygen demand curves, there is in fact, relatively little difference between the various criteria. With regard to the oxygen demand, if adequate provision for the daily peak demand is incorporated in the design, it is very likely that the application of any one set of criteria will result in satisfactory plant operation under the design loads. For example in the procedures of Metcalf and Eddy, although the oxygen demand is significantly lower than that proposed by the theory in this paper, American practice requires an oxygen supply of 50 percent greater than the steady state requirements, whereas the theoretical dynamic behaviour suggests a 30 percent increase. The final oxygen provision comes out to be about the same.

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REFERENCES

ANDERSON, G.K., (1973): "Aerobic Biological Water Treatment – Application of Process Theory", *Lecture Notes, Div. of Public Health, Dept. of Civil Eng.*, Univ. of Newcastle upon Tyne.

ANDREWS, J.F. and BUSBY, J.R., (1973): "Dynamic Modelling and control Strategies for the Activated Sludge Process", *Res. Rept., Dept. of Environ. Systems Eng.*, Clemson Univ., Clemson, S. Carolina.

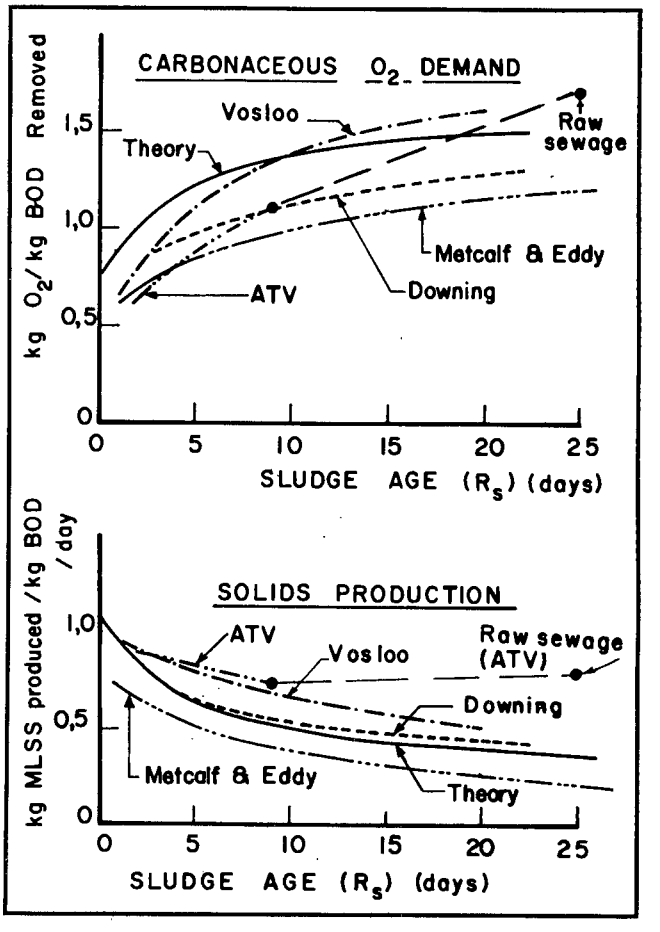

Figure 29
Comparison of design criteria for oxygen demand and sludge production per day

BARNARD, J. L., (1973): "Biological Dentrification", *Water Pollut. Contr.*, 72, 6, 705-720.
BARNARD, J. L., (1975): "Nutrient Removal in Biological Systems", *Water Pollut. Contr.*, 74, 143-154.
BARTH, F., BRENNER, R.C. and LEWIS, R.F., (1968): "Combined Chemical and Biological Control of Nitrogen and Phosphorus in Wastewater Effluent", *J. Wat. Pollut. Control Fed.*, 40, 12, 2040-2054.
BOON, A.G. and BURGESS, D.R., (1972): "Effects of Diurnal Variations of Flow of Settled Sewage on the Performance of High Rate Activated Sludge Plants", *Water Pollut. Contr.*, 6, 493.
BRATBY, J. and MARAIS, G. v. R., (1976): "A Guide for the Design of Dissolved-air (Pressure) Flotation Systems for Activated Sludge Processes", *Water SA*, Vol 2, No 2, 86–100.
DIXON, H., BELL. B. and AXTELL, R.J., (1972): "Design and Operation of the Works of the Basingstoke Department of Water Pollution Control", *Water Pollut. Contr.*, 72, 2, 167.
DOWNING. A.L., (1968): "Factors to be considered in the Design of Activated Sludge Plants". In: *Advances in Water Quality Improvement.* Eds. Gloyna and Eckenfelder, Univ. of Texas Press, p. 190.
DOWNING, A.L., PAINTER, H.A. and KNOWLES, G., (1964): "Nitrification in the Activated Sludge Process", *J. Proc. Inst. Sew. Purif.*, 64, 2, 130.
ECKENFELDER, W.W., (1967): "Comparative Biological Waste Treatment Design", *J. Sanit. Eng. Div.*, Am. Soc. Civ. Engrs., 93, SA6, 157.
ECKENFELDER, W.W. and WESTON, R.F., (1956): "Kinetics of Biological Oxidation". In: *Biological Treatment of Sewage and Industrial Wastes*, Vol. 1, Eds. B.J. McCabe and W.W. Eckenfelder, Rheinhold Publ. Co., New York, p. 18-34.
EKAMA, G.A. and MARAIS, G. v. R., (1975): "The Activated Sludge Process, Pt. II – Dynamic Behaviour", *Res. Rept. No. W. 13, Dept. of Civil Eng.*, Univ. of Cape Town.
GARRET, M.T. Jr.,(1958): "Hydraulic Control of Activated Sludge Growth Rate", Sew. and Indus. Wastes, 30, 253.
GARRET, M.T. Jr.,(1972): "Discussion on 'A Consolidated Approach to Activated Sludge Process Design'" by B.L. Goodman and A.J. Englande, Proc. Biol. Waste Treat. Confr., Atlanta.
GAUDY, A.F., OBAYASHI, O. and GAUDY, E.T., (1971): "Control of Growth Rate by Initial Substrate Concentration at Values below Maximum Rate", *App. Microbiology*, 22, 1041-1047.
GOODMAN, B.L. and ENGLANDE, A.J., (1972): "A Consolidated Approach to Activated Sludge Process Design", Proc. Biol. Waste Treat. Confr., Atlanta.
HEUKELEKAIN, H., OXFORD, H. E. and MANQUNELLI, R., (1951): "Factors Affecting the Quantity of Sludge Production in the Activated Sludge Process", Sew. and Indus. Wastes, 23, 8. 945.
HOPWOOD, A.P., and DOWNING, A.L., (1965): "Factors Affecting the rate of Production and Properties of Activated Sludge in Plants Treating Domestic Sewage", *J. Inst. Sew. Purif.*, Pt. 5, 435.
JENKINS, S.H, KNIGHT, D.G., SNADDEN, X.V.M. and JAMES, K., (1967): "Large Scale Experiments on the Treatment of Sewage at Minworth Works from 1961 to 1966", *Water Pollut. Contr.*, 66, 334-366.
LAWRENCE, A.W. and MCCARTY, P.L., (1970): "Unified Basic for Biological Treatment Design and Operation", *J. Sanit. Eng. Div.*, Am. Soc. Civ. Engrs., 96, SA3, 757-778.
MARAIS, G. v. R.,(1974): "Feacal Bacterial Kinetics in Stabilization Ponds", *J. Envir. Eng. Div.*, ASCE, 100, EE1, 119-139.
MARAIS, G. v. R., (1973): "The Activated Sludge Process at Long Sludge Ages", *Res. Rept. No. W3.* Dept. of Civil Eng., Univ. of Cape Town.
MARSDEN, M.G. and GOLOI, V.P.,(1973): "VSS to COD Ratio", *Undergraduate Report*, Dept. of Civil Eng., Univ. of Cape Town.
MCKINNEY, R.E.,(1962): "Mathematics of Complete-mixing Activated Sludge", *J. San. Eng. Div.*, ASCE, SA3, 88.
MCKINNEY, R.E., and OOTEN, R.J., (1969): "Concepts of Complete Mixing Activated Sludge", Trans. 19th Eng. Confr., Univ. of Kansas, 32.
METCALF and EDDY, (1972): "*Waste Water Engineering*, 1st Edition, McGraw Hill, New York.
MONOD, J.,(1950): "Technique of Continuous Culture – Theory and Application" (Translation from French), Ann. Inst. Pasteur, 79, 167.
NICHOLLS, H.A.,(1975): Internal Thesis Report, Dept. of Civil Eng. Univ. of Cape Town.
PITMAN, A.R.,(1974): "Bioflocculation as a means of improving the Dewaterability of Activated Sludge", Paper delivered to Inst. Water Pollut. Contr., S.A. Branch, Johannesburg.
PORGES, N., JASEWICS, L. and HOOVER, S.R.,(1956): "Principles of Biological Oxidation" In: *Biological Treatment of Sewage and Industrial Wastes*, Vol. 1, Eds. B.J. McCabe and W.W. Eckenfelder, Rheinhold Publ. Co., New York, p. 35-48.
SERVIZI, J.A. and BOGAN, R.H.,(1963): "Free Energy as a Parameter in Biological Treatment", *J. San. Eng. Div.*, ASCE, SA3, 63.
STERN, L.B. and MARAIS, G. v. R., (1974): "Sewage as Electron Donor in Biological Denitrification". *Res. Rept. No. W7*, Dept. of Civil Eng., Univ. of Cape Town.

Appendix A

Comparison of the McKinney and the Lawrence and McCarty Models for the Activated Sludge Process

No satisfactory theoretical comparison between the two models has been put forward. At first sight, the process equations derived from the two theories appear so different that there is a tendency to accept that their application will lead to very different process designs.

In order to make a rational comparison between the two theories it is necessary to reduce the process equations to equivalent forms. With this objective in mind the Lawrence and McCarty equation is accepted as the basis for comparison.

In the text of this paper the Lawrence and McCarty model has been extensively discussed and the following pivotal equations derived for the long sludge age approximation.

$$dX_a/dt = YKSX_a \quad (1A)$$

$$dS/dt = KSX_a \quad (2A)$$

Applying these equations in the CMAS system the following steady state equations were established:

$$1/R_s = YKS - b \quad (3A)$$

$$X_a = \frac{Y(S_i - S)}{1 + bR_s} \cdot \frac{R_s}{R} \quad (4A)$$

McKinney (1962) and McKinney and Ooten (1969) postulated that under the same conditions governing Eqs. (1A) and (2A) above, the rate of synthesis of active mass concentrations is a *function only of the substrate concentration*, i.e.

$$dX_a/dt = K'_s S \quad (5A)$$

K'_s is a constant for a particular waste called the "synthesis factor" for it is associated with the synthesis of organisms from the substrate.

They further postulated that the mass of organisms synthesized is proportional to the mass of substrate utilized so that the rate constants K'_s and K'_m must be related to the yield facsimilar to Eq. (5A), i.e.

$$dS/dt = K'_m S \quad (6A)$$

K'_m is a constant for a particular waste; it is called the "metabolism factor" because the substrate which disappears is utilized in the metabolic process of the organisms, for the actual synthesis and for energy to synthesize. As the mass synthesized is proportional to the mass of nutrient utilized, this implies that the rate constants K'_s and K'_m must be related to the yield factor Y, as follows:

$$dX_a/dt = YdS/dt \quad (7A)$$

or

$$dX_a = YdS \quad (8A)$$

Substituting Eqs. (5A) and (6A) in Eq. (7A) yields:

$$K'_s S = YK'_m S$$

i.e.

$$Y = K'_s/K'_m \quad (9A)$$

Referring to Fig. 3 in the text, a substrate balance yields

$$V\frac{dS}{dt} = K'_m SV + S_i Q - SQ$$

Dividing by V, noting that V/Q = R, equating to zero for steady state and solving for S:

$$S = S_i/(K'_m R + 1) \qquad (10A)$$

A solids balance on X_a yields:

$$VdX_a = K'_s SVdt - bX_a Vdt - qX_a dt \qquad (11A)$$

Dividing by Vdt, equating to zero for steady state and noting that V/q = R_s and V/Q = R

$$X_a = \frac{K'_s S}{b + 1/R_s} = \frac{K'_s SR}{1 + bR_s} \qquad (12A)$$

Eqs. (10A) and (12A) are the basic process equations derived by McKinney and should be compared with the corresponding Eqs. (3A and 4A) of Lawrence and McCarty.

A comparison of the two theories is made easier by reducing the relevant equations to equivalent forms. For this purpose Eqs. (3A and 4A) of Lawrence and McCarty are selected as the basis for comparison. McKinney's equations can be reduced to equivalent forms as follows:

Eq. (10A) can be written

$$S = \frac{S_i - S}{K'_m R}$$

Substituting in Eq. (12A) and reducing

$$X_a = \frac{K'_s}{K'_m}\frac{(S_i - S)}{1 + bR_s}\frac{R_s}{R} \qquad (13A)$$

Substituting Eq. (9A) in Eq. (13A)

$$X_a = Y\frac{(S_i - S)}{1 + bR_s}\frac{R_s}{R} \qquad (14A)$$

Eq. (14A) is identical to Eq. (4A) derived by Lawrence and McCarty.

In Eq. (12A) solving for $1/R_s$

$$1/R_s = \frac{K'_s}{X_a}S - b$$

Substituting from Eq. (9A)

$$1/R_s = Y(K'_m/X_a)S - b \qquad (15A)$$

Eq. (15A) is similar in form to Eq. (3A) derived by Lawrence and McCarty. For compatibility between Eqs. (3A) and (15A) it is necessary that

$$K'_m/X_a = K$$

Now X_a is not a constant, hence if K is to be a constant (as postulated by Lawrence and McCarty) then K'_m necessarily cannot be a constant (as postulated by McKinney) but must be proportional to X_a; furthermore, if Y is a constant then both K'_m and K'_s must be variables. In this event, the 'constants' K'_m and K'_s in Eqs. (10A) and (12A) respectively are variables. Alternatively, if K'_m is a constant (as postulated by McKinney) then K must necessarily be a variable for compatibility. The two theories are therefore incompatible.

If the assumption is valid that K'_s/K'_m = Y is a constant, then Eqs. (4A) and (13A) are identical, but Eqs. (3A) and (15A) are then not necessarily so. Thus one obtains compatibility between the two theories insofar as they relate to sludge production, but not insofar as they relate to effluent quality. This is not unexpected as Eq. (13A) requires knowledge of the value of S but is not involved in the determination of S, a situation exactly the same as Lawrence and McCarty's theory [(Eq. 4A)]. It is in the determination of S where the crucial difference between the two theories lies.

Is this difference of practical importance? The *relative* values of S as determined by the two theories may differ by several hundred percent, but the *absolute* difference is, in fact, negligible because the values of S in both theories are usually very low. Consequently, the calculation of X_a from Eq. (14A), utilizing either Eq. (3A) or Eq. (10A) to determine S, leads to negligible differences in the active sludge mass concentrations.

Although the practical effect of using the two theories is a negligible difference in both the active mass concentrations and the effluent quality, the conceptual difference is of prime importance: In McKinney's theory the effluent quality, S, is solely a function of the retention time, [(Eq. 10A)], the sludge age being immaterial, whereas in Lawrence and McCarty's theory the effluent quality is solely a function of the sludge age [(Eq. 3A)], the retention time being immaterial.

Appendix B

Aerobic Digestion with Dentrification

Consideration will be given only to a single stage aerobic digestor having a dentrification stage. The configuration is given in Fig. 1B. The contents of the digestor are nitrified in reactor 2 and recycled to the anoxic reactor (which also receives the influent flow). In anoxic reactor 1 the nitrified digestor content is denitrified.

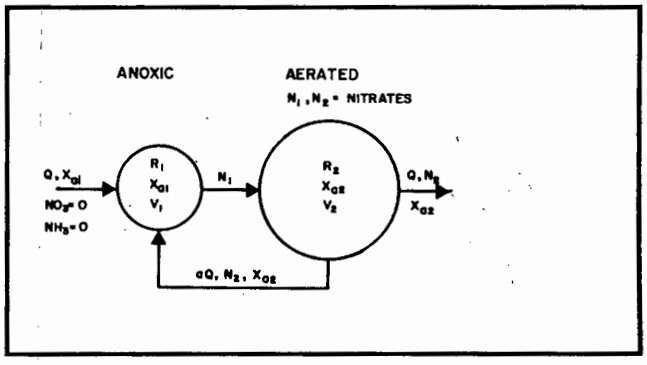

Figure 1B
Proposed process for aerobic digestion with denitrification

The reduction of active mass through this system can be modelled directly by the theory on the die-off of feacal bacteria, proposed by Marais (1974). Basic assumption (for our purpose) is that endogenous mass loss continues under anoxic conditions at the same rate as under aerobic conditions, Stern and Marais (1974). The following sequence of equations is required:

$$X_{a2} = X_{ai}/J \tag{1B}$$

where $$J = \frac{(bR_1 + a + 1)(bR_2 + a + 1)}{a + 1} - a$$

$$X_{a1} = \frac{X_{ai} + aX_{a2}}{bR_1 + a + 1} \tag{2B}$$

Equations (1B and 2B) relate the concentrations in the two reactors to the retention times R_1 and R_2, and the recycle rate, a. Initially R_1, to give optimal nitrate removal, is unknown. The problem is amenable to direct solution, but this is so complex that it is not practical. An alternative approach is a trial method which is best explained by means of an example:

Influent X_{ai} = 10 000 mg/ℓ, total retention time of system selected as 15 days. Design the system to give 90% reduction of nitrates generated. Temperature 20°C, i.e. b = 0,24.

Recycle required

The retention time in the anoxic reactor must be sufficient to reduce all the nitrate recycled to it, i.e. N_2 = O. Also, as the nitrate is formed in the aerobic digestor reactor it is not possible to remove the nitrate completely as the effluent and recycle flows have the same nitrate concentration. Say x percent is to be removed then recycle, a, must have a value given by:

$$\frac{a}{a + 1} = \frac{100 - x}{100} \tag{3B}$$

i.e. if x is 90 percent, a = 9.

Anoxic reactor retention time

At recycle rates a ≥ 6, X_{a1} and X_{a2} will not differ greatly. This approximate equality provides a means for estimating R_1.

Assume $X_{a1} = X_{a2} = X_a$, the concentration from a single aerobic reactor with 15 days retention. Then from Eq. (90):

$$X_a = \frac{10\,000}{0{,}24.15 + 1} = 2174 \text{ mg/ℓ}$$

Nitrate generated (Eq. 98) = $(X_{ai} - X_a)0{,}8.0{,}1$ = 626 mg/ℓ. Nitrate available for dentrification, N_2, (using a recycle of a = 9) = 0,9.626 = 563 mg/ℓ NO_3–N.

Doing a mass balance for the nitrates on the anoxic reactor, remembering that N_1 = 0 (Stern and Marais, 1974):

$$\Delta N_2 = K R_1 X_a \tag{4B}$$

where ΔN_2 = system nitrate removal, mg/ℓ
R_1 = nominal retention time of anoxic reactor (V/Q), days
K = endogenous respiration dentrification rate, 0,055 mg NO_3–N)mg MLVASS/d at 20°C (Stern and Marais, 1974)

i.e.

$$R_1 = \frac{N_2}{KX_a} \tag{5B}$$

$$= \frac{9.563}{0{,}055.2174} = 4{,}7 \text{ d, say 4 d.}$$

It is now possible to check the design by means of the exact equations.

From Eqs. (1B and 5B), substituting R_1 = 4, R_2 = 11, a = 9, and X_{ai} = 10 000, we have X_{a2} = 2062, X_{a1} = 2605.

Nitrate generated = $0{,}08(X_{ai} - X_{a2})$ = (10 000 – 2062)0,08
= 635

Nitrate to be removed = 635.0,9 = 572 mg/ℓ

Nitrate removal potential = $KX_{ai}R$ = 0,55.2605.4
= 573

which, in this case, is just satisfactory.

The period an organism is under a continuous anoxic state in the anoxic reactor, R_{1a}, is given by:

$$R_{1a} = \frac{R_1}{(a + 1)}.24 = \frac{4}{10}.24 = 9{,}6 \text{ hr.} \tag{6B}$$

Effluent nitrate concentration = 0,1.635 = 63,5 mg/ℓ.

Lime addition may still be required to keep the pH above 7.

If phosphorus removal is more important than nitrate removal, lime addition to the reactor without an anoxic stage may be preferable. The lime will be neutralized to $Ca(NO_3)_2$ and if the pH is maintained at above 8, calcium phosphate should be precipitated as the Ca^{++} ions are increased considerably, to exceed the [Ca] [PO_4] solubility product.

The oxygen requirements could be calculated from the theory given in the paper.

The theoretical considerations above have not been tested experimentally.

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A GENERAL MODEL FOR THE ACTIVATED SLUDGE PROCESS

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Abstract

A comparison of experimental data with those predicted by the mathematical model of Ekama and Marais (1978) describing the dynamic behaviour of the completely mixed activated sludge (CMAS) process, indicated that certain hypotheses in this model needed replacement. The following principal changes were made: (1) The energy requirement for adsorption was replaced by a bi-substrate hypothesis. In this hypothesis municipal wastewaters are taken to consist of two substrates - a rapidly biodegradable soluble and a slowly biodegradable particulate substrate. The growth behaviour of the former is in accordance with the classical Monod (1950) formulation; while the growth behaviour of the latter is controlled by the rate of extracellular enzymatic breakdown of the large complex molecules to simpler ones before transference through the cell walls. (2) The extracellular growth-limiting reaction is modelled by an active site theory and replaces the modified Blackwell (1971) equation for synthesis of stored particulate substrate. (3) The classical endogenous respiration concept is replaced by a death-regeneration one. Incorporation of these concepts in the CMAS process equations give excellent description of the process behaviour (oxygen utilization rate, volatile solids production, COD, TKN, nitrate) under constant and cyclic flow and load conditions for single and multiple reactor configurations. The model allows extension to the single sludge nitrification-denitrification and the contact stabilization processes although these are not discussed in this paper.

INTRODUCTION

In 1979, Ekama and Marais presented a dynamic model for the aerobic activated sludge process, including nitrification. This model gave a good description of the response of single and series reactor process configurations under steady and cyclic loading conditions at different temperatures. Further research on the model indicated that it appeared to be amenable to extension to both the contact stabilization activated sludge process and the single sludge nitrification-denitrification activated sludge process utilizing the influent COD as energy source. In developing these extensions it became clear that there were deficiencies in the basic model but from

an interactive development of the three processes, a modified kinetic theory was evolved. This modified theory appears to be of greater generality and allows the integration of the aerobic and anoxic-aerobic activated sludge processes.

This paper describes the modifications to the basic kinetic relationships, and application of the modified model to aerobic single and series reactor configurations under steady and cyclic loading conditions. Application of the modified model to the contact stabilization and anoxic-aerobic systems include features peculiar to these processes and is discussed in separate papers.

DESCRIPTION OF THE ORIGINAL MODEL

Carbonaceous Energy Removal

The Marais and Ekama (1976) model was developed from that of Lawrence and McCarty (1970). The latters' model accepted the Monod equation which relates the specific organism growth rate with the concentration of substrate surrounding the organism. They also accepted that, concomitant with growth, there is a continuous loss of volatile mass (endogenous respiration) at a constant specific rate with respect to the volatile mass. In terms of these basic biological reactions, Lawrence and McCarty (1970) developed the equations for the behaviour of the completely mixed activated sludge (CMAS) process under steady state conditions for determination of the effluent and sludge concentrations.

Marais and Ekama (1976) incorporated into the Lawrence and McCarty model some of the concepts proposed earlier by McKinney (1962), i.e. the generation of endogenous residue due to endogenous respiration and the accumulation of inert volatile solids due to the presence of this material in the influent. Furthermore, on the basis of a constant equivalence between organic mass (VSS) and substrate (COD), they functionally integrated the oxygen consumption with the growth and endogenous respiration.

The major advantage of the Marais and Ekama (1976) model is that it (1) distinguishes between the active and inert sludge fractions, (2) expresses the biological reactions in terms of active mass, and (3) allows the oxygen utilization rate to be determined directly from the biological reactions. Application of this modified model to the single reactor CMAS process with domestic wastewater as influent under constant load and flow conditions gave a very good description of the process behaviour over a range of sludge ages and temperatures. Later (Ekama and Marais, 1978) this model was also found to give a good correlation between predicted and experimental data when square wave cyclic loading conditions were imposed on the process with glucose as influent substrate (Fig. 1). An important consequence of this work was a recognition of the oxygen utilization rate as a most sensitive parameter against which the activated sludge theory can be tested.

In 1979, Ekama and Marais applied the model to cyclically loaded CMAS processes receiving domestic wastewater as influent. At low sludge ages (R_S = 2,5 days) it was found impossible to correlate the predicted and observed oxygen consumption rates (Fig. 2). At the instant of feed termination a precipitous change in the oxygen consumption rate was observed, thereafter the rate continued for 1,5 to 2 hours at a rate of about 90 per cent of that measured just before the feed terminated; this was followed by a period of approximately 5 hours during which the oxygen consumption rate gradually decreased until, fairly abruptly, the rate steadied at a value which could be associated with endogenous respiration.

Ekama and Marais ascribed the difference between the observed and predicted response to the nature of the influent substrate: In domestic waste flows 60 to 70 per cent of the COD is in a fine particulate form (Morris and Stumm, 1960; Ford and Eckenfelder, 1967; Wilson and Marais, 1976). The utilization of particulate

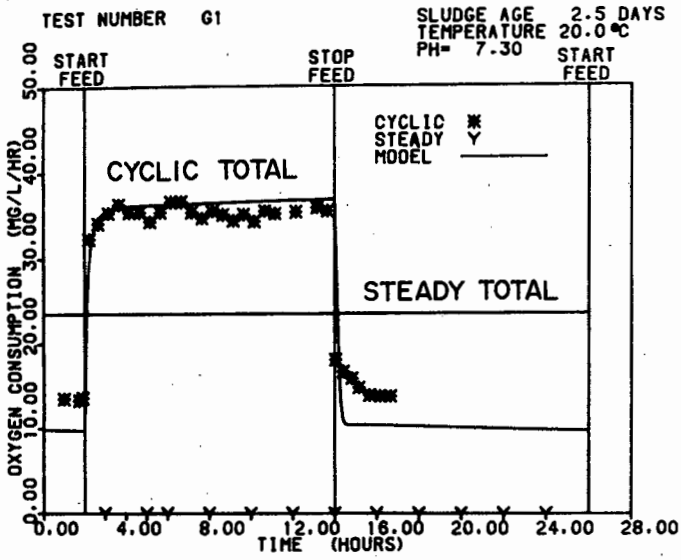

Fig. 1. Comparison of the theoretical response waves predicted by the Marais and Ekama (1976) model with those observed experimentally for daily cyclic square wave loading conditions at 2,5 days sludge age and temperature 20°C, with glucose as substrate.

substrate necessarily requires to be preceded by adsorption and storage on the organism, followed by extracellular enzymatic breakdown prior to transfer through the cell wall. Hence, they incorporated an adsorption mechanism to store the particulate biodegradable material on the organism. The adsorption mechanism they adopted was a modification of that proposed by Blackwell (1971), the modified formulation being:

$$\frac{dS_b}{dt} = - K_a S_b X_a (f_{ma} - X_s/X_a) \qquad (1)$$

where

K_a = substrate transfer rate (mg COD/mg VASS/d)

X_a = active volatile solids concentration (mg VASS/ℓ)

S_b = biodegradable substrate concentration in the liquid phase (mg COD/ℓ)

X_s = stored substrate concentration (mg VSS/ℓ)

f_{ma} = maximum fraction of substrate than can be stored on the active organism mass (mg VSS/ mg VASS)

To explain the precipitous drop in oxygen consumption rate at feed termination, Ekama and Marais (1979) hypothesized that this may be due to an energy requirement for carbonaceous substrate adsorption. They further hypothesized that all the biodegradable COD in the domestic wastewater can be taken to be of a particulate nature; even though approximately 30 per cent of the COD is not removed by filtration, it is likely that the filtrate COD consists of large complex organic

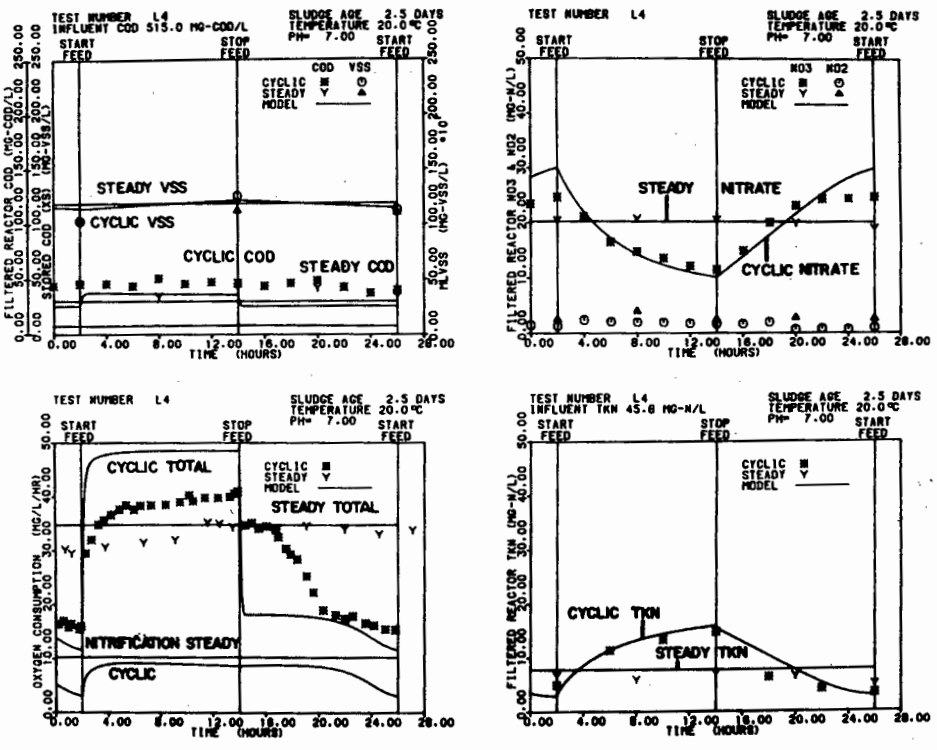

Fig. 2. Comparison of the theoretical response waves predicted by the Marais and Ekama (1976) model with those observed experimentally for daily cyclic square wave loading conditions at 2,5 days sludge age, pH 7,0 and temperature 20°C.

molecules which also require extracellular enzymatic breakdown. Consequently, they accepted that all biodegradable COD must pass through the adsorption and storage phase. Having accepted the hypothesis that biological adsorption is an energy demanding reaction, they utilized the step change in oxygen consumption rate to determine the energy required for adsorption and storage of COD, and calculated it to be 7,8 per cent of the COD mass removed from the bulk phase.

Utilization of the stored substrate for synthesis was modelled by a Monod type relationship linking the stored substrate concentration to the specific growth rate of the active organisms, i.e.

$$\frac{1}{X_a}\frac{dX_a}{dt} = Y_h\left[\frac{K_m X_s P}{K_s + X_s P}\right] \qquad (2)$$

where

Y_h = growth yield coefficient in terms of stored substrate as mg COD/ℓ (mg VSS/mg COD)

K_m = maximum specific substrate utilization rate (mg COD/mg VSS/d)

K_s = half saturation coefficient (mg COD/ℓ)

P = COD:VSS ratio (mg COD/mg VSS)

This relationship had been proposed by a number of previous investigators (Blackwell, 1971; Jacquart, Lefort and Rovel, 1973; and Busby and Andrews, 1973) and Ekama and Marais found it adequate for modelling the synthesis of stored COD reaction.

Nitrification

The Ekama and Marais (1979) model for biological nitrification was based on the model proposed by Downing, Painter and Knowles (1964). In this model the Monod formulation is used to relate the ammonia substrate concentration to the specific growth rate of the nitrifying bacteria. However, the Downing model does not consider the effect of the presence of organic nitrogen on the nitrification kinetics. The incorporation of the influence of organic nitrogen into the model required two extensions:

1. It was necessary to include a conversion of the organic nitrogen derived from the influent and from endogenous mass loss to ammonia, a relatively slow reaction. This explains the experimental observation that, in certain situations, the nitrification rate is apparently no longer governed by the ammonia concentration, but rather by the rate of conversion of organic nitrogen to ammonia,

2. Storage of COD necessitated the inclusion of storage of organic nitrogen.

With these modification, the model was found to give a satisfactory correspondence with TKN, ammonia and nitrate concentrations observed during daily cyclic square wave loading tests.

MODIFICATIONS TO THE MODEL

Criticism of the Ekama and Marais (1979) model will be discussed under a number of headings:

Energy Demand for Adsorption

Thermodynamically, the adsorbed state is associated with a lower energy level than the unadsorbed one. Should this be true also for the biologically mediated adsorption of organic material onto the organisms, the hypothesis that the adsorption is energy demanding would appear to be suspect. This doubt was reinforced subsequently when experiments on CMAS behaviour using a soluble, easily biodegradable substrate (glucose) were performed. Under square wave cyclic loading conditions the oxygen utilization rate showed a precipitous decrease at feed termination and generally the response of the plant was in accordance with the predictions of the modified Lawrence and McCarty model, (Fig. 1). These pure substrate expreiments led to the hypothesis that municipal wastewater is composed of two fractions: (a) a readily assimilable soluble fraction which is utilized at a very rapid rate, and (b) a slowly biodegradable particulate fraction which requires storage and enzymatic breakdown prior to transfer through the cell wall. In terms of this hypothesis the step change in the oxygen consumption rate at feed termination using municipal wastewater, (Fig. 2), may be attributed to the cessation of the oxygen utilization for the metabolism of the rapidly biodegradable substrate (COD) fraction in the influent. Subsequent to the step change the behaviour remains a consequence of the storage of COD derived from the particulate, slowly biodegradable portion of the influent - indeed the mechanism of adsorption and storage of particulate COD remains unchanged, except that this operates on only the particulate fraction of the influent and does not require energy for adsorption.

In order to simulate the step change at feed termination with the bisubstrate hypothesis, approximately 24 per cent of the biodegradable COD in the influent necessarily must be readily assimilable. This was developed as follows: In the

synthesis reaction the oxygen requirement constitutes 34 per cent of the COD metabolized; the balance, i.e. 66 per cent, becomes new cell mass (Marais and Ekama, 1976). The fraction of the biodegradable influent COD which is rapidly assimilable therefore, is 1/0,34 times the size of the step change in the oxygen utilization rate, i.e. 0,08/0,34 = 0,24. This fraction is not unreasonable when it is noted that 30 to 40 per cent of the COD in domestic wastewater is apparently soluble.

Rôle of Adsorption

Adsorption is an example of a mass transfer process and its formulation, as expressed in Eq. (1) is in conformity with mass transfer principles. For this reason there appeared to be no need to reconsider its formulation, i.e. Eq. (1) was retained.

Rôle of Enmeshment

From the behaviour of the experimental CMAS process the complete insensitivity of the effluent COD to severe cyclic load variations could not be explained by the adsorption hypothesis alone. It was necessary to make an additional hypothesis that all the particulate material not adsorbed was enmeshed in the sludge mass, densified in the settling tank and recycled to the reactor. This hypothesis has powerful support from the observation that inert particular material does not appear in the overflow from the settling tank.

Synthesis of Active Mass

Acceptance of a bi-substrate hypothesis immediately introduces the problem of the reaction of the organism mass to the two substrates. The exact mechanism cannot yet be stated explicitly but, from an extensive simulation study, it appears that the two substrates are acted on independently by the same active mass and that the sludge synthesized is the sum of these two metabolic reactions.

Soluble substrate. The synthesis of active mass from the readily assimilable substrate fraction was formulated identically to that of Lawrence and McCarty (1970) i.e. a Monod relationship linking the specific growth rate of the active mass to the soluble substrate concentration in the liquid phase:

$$\frac{1}{X_a}\frac{dX_a}{dt} = Y_h\left[\frac{K_{ms}S_{bs}}{K_{ss}+S_{bs}}\right] \qquad (3)$$

where

S_{bs} = soluble biodegradable substrate concentration (mg COD/ℓ)

K_{ms} = maximum specific substrate utilization rate for souble substrate (mg COD/mg VSS/d)

K_{ss} = half-saturation coefficient for soluble substrate (mg COD/ℓ)

Gaudy, Obayshi and Gaudy (1971) have criticised this relationship as inappropriate for modelling transient behaviour of the activated sludge process treating readily assimilable soluble substrates: they found that the relationship did not accurately predict the change in organism growth behaviour for a period after a step change in the feed rate.

The behaviour observed by Gaudy, Obayshi and Gaudy can perhaps be attributed to differences in the experimental conditions: They were concerned with the transient behaviour between two steady state conditions where, over the duration of an experiment, the change in the food to micro-organism ratio was in the order of 170 times.

In contrast, the activated sludge process is usually concerned with comparatively small perturbations about a steady state condition, in which the peak food to micro-organism ratio is at most 5 times the average value.

Particulate substrate. Utilization of particulate substrate requires (1) adsorption and storage, (2) extracellular enzymatic breakdown of the complex organic molecules to simpler ones in order to pass through the cell wall for (3) synthesis by the organism. The overall reaction rate is slow - an order of magnitude slower than that for a soluble substrate such as glucose. The limiting rate is unlikely to be in the metabolism of the material that has passed through the cell wall, for that material is probably of a similar nature to glucose and consequently is metabolized at a very rapid rate. More likely, the limiting rate is determined by the rate of extracellular breakdown of stored particulate substrate to smaller molecular units. If this explanation is accepted, then Eq. (2) is no longer appropriate to formulate the growth rate of the active mass when utilizing particulate substrate as it does not take cognizance of the true rate limiting mechanism namely, the rate of extracellular enzymatic breakdown. Equation (2) can be justified only by reason that its use has given satisfactory predictions of the dynamic behaviour of the CMAS process treating domestic wastewater. However, this justification now can be shown to be no longer valid: When applied in simulations of the BOD-time curve in the BOD test on municipal effluents, where the initial active mass concentration is very small (probably << 1 mg /ℓ), virtually no growth (and no oxygen demand) and no removal of the particulate biodegradable organic fraction in the BOD sample was predicted for the utilization of the particulate BOD. Also, when Eq. (2) was applied in the prediction of the behaviour of the aerated lagoon activated sludge process, at sludge ages (retention times) less than two days and low temperatures (12°C), a behavioural pattern was predicted that indicated an insufficient sludge growth rate and partial failure by washout.

An in-depth study of the anomalous behaviour described above indicated that it arises from Eq. (2): The adsorption and synthesis mechanisms (Eqs. 1 and 2) respectively, operate in conjunction. From Eq. (1) it is apparent that the stored substrate concentration (X_s) is restricted by the active mass concentration (X_a) and the value of the maximum fraction of substrate that can be stored on the active organism mass (f_{ma}). From simulation studies and evidence in the literature (Porges, Jasewicz and Hoover, 1952), f_{ma} appears to have a value approximating unity. Consequently when X_a is low, X_s is necessarily also low and from Eq. (2) the synthesis rate also will be low. This is contrary to expectation, for, in such a situation the growth rate should be close to the maximum because there is a large amount of X_s relative to X_a. This deficiency stems from the fact that the stored substrate is defined in concentration units relative to the bulk liquid phase. Preferably, it should be defined relative to the active organism concentration. Stenstrom (1975) recognized this deficiency and suggested the following modification:

$$\frac{1}{X_a}\frac{dX_a}{dt} = Y_h\left[\frac{K_m(X_s/X_v)}{K_{fs} + (X_s/X_v)}\right] = Y_h\left[\frac{K_m f_s}{K_{fs} + f_s}\right] \qquad (4)$$

where

f_s = X_s/X_v (mg VSS/mg VSS)

K_{fs} = half saturation coefficient for synthesis (mg VSS/mg VSS)

X_v = total volatile solids concentration (mg VSS/ℓ)

By accepting Eq. (4) a more rational formulation is achieved, but now the relationship is completely empirically based. For this reason an alternative approach, to

formulate the synthesis rate limiting equation in terms of surface mediated reactions was sought. Levenspiel (1972)proposed that such reactions may be modelled in terms of the number of adsorption sites that are saturated by means of a saturation type relationship as follows:

$$r_a = K_1 C_{as}/(K_2 + C_{as}) \quad (5)$$

where

r_a = reaction rate

K_1, K_2 = constants

C_{as} = concentration of reactant at the active surface in moles/unit area.

Applying Eq. (5) to the extracellular reaction, the stored substrate per unit area of active mass may be approximated by $(X_s/X_a)^n$, where n depends on the volume to surface area ratio of the active mass, the equation for the synthesis reaction becomes:

$$\frac{1}{X_a}\frac{dX_a}{dt} = Y_h\left[\frac{K'_{mp}(X_s/X_a)^n}{K'_{sp}/P + (X_s/X_a)^n}\right] \quad (6)$$

where

K'_{mp} = maximum specific substrate utilization rate using stored substrate (mg COD/mg VSS/d)

K'_{sp} = half-saturation coefficient (mg COD/mg VSS)

n = factor depending on the volume to surface area ratio for the active mass.

If the active mass is assumed to be a planar surface, then n = 1, if a spherical surface, than n = 2/3. However, different values of n resulted in inconsequential differences in the theoretical predictions of the mathematical model, when compared with the experimental observations. Consequently, it was accepted that the active mass adsorption surface is planar, i.e. n = 1. Equation (6) may then be reduced to:

$$\frac{1}{X_a}\frac{dX_a}{dt} = Y_h\left[\frac{K'_{mp}(X_s/X_a)}{(K'_{sp}/P) + (X_s/X_a)}\right] \quad (7)$$

Equation (7) is of the same structure as that of Stenstrom (Eq. 6) except that the term (X_S/X_a) in Eq. (7) replaces (X_S/X_v) in Eq. (6). This modification is, in fact, rational for the active sites are present only on the active mass fraction of the sludge. Thus, by utilizing surface reaction mechanism a rate limiting equation for synthesis of particulate biodegradable substrate can be established.

When Eq. (7) was incorporated in the mathematical model, application of the model to the suspension mixed aerated lagoon indicated an acceptably high sludge growth rate even at retention times as low as 12 hours. Similarly, a significant improvement in predictions of the BOD-time curve was obtained. Equation (7) therefore was accepted as the rate equation for synthesis of particulate biodegradable substrate.

Endogenous Respiration

The phenomenon commonly known as endogenous respiration manifests itself by a reduction of active volatile mass per unit active mass per unit time when there is no biodegradable substrate present.The mass of sludge mass that disappears is

utilized by the organisms and therefore is directly equated to the oxygen consumption for endogenous respiration. An unbiodegradable fraction remains, and accumulates in the process as endogenous residue.

Endogenous respiration has been attributed to an energy requirement for organism maintenance, where a fraction of the organism mass disappears to provide energy for maintenance of the mass remaining. In order to make the energy available an electron acceptor must be present; in the activated sludge process, either oxygen or nitrate can serve as the electron acceptor. A major problem in modelling the single sludge nitrification-denitrification process was encountered in situations where both the oxygen and nitrate concentrations in a reactor are zero, for example when nitrate has been completely denitrified in an anoxic reactor. When no oxygen or nitrate is present, maintenance energy cannot be released. What happens to the organism under these circumstances?

Dissolved oxygen and nitrate deficient conditions can be accommodated by introducing a qualitative change in organism behavioural pattern. However, this presented complications in the model which hardly seemed justified when the basic endogenous respiration mechanism was not clearly delineated. Consequently, the objective became to find a simple alternative model which could rationally answer the inconsistencies regarding endogenous respiration in both aerobic and anoxic conditions, and also in situations where aerobically generated organisms are placed in an anaerobic state for a short period. This led to the development of the death-regeneration model.

In the death-regeneration model an attempt is made to separate out reactions which possibly take place during the "death phase" of the organisms. It is hypothesized that the percentage of live mass that disappears in fact dies, lyse biodegradable substrate back into the liquid, and leaves the balance as unbiodegradable endogenous residue. The lysed biodegradable substrate is added to the biodegradable COD in the liquid and passes through the same phases of adsorption, storage and storage abstraction for synthesis. This approach, in effect, implies that endogenous respiration (cell maintenance) *per se* does not exist and that oxygen is consumed only for synthesis of new cell material from the lysed energy. By appropriate selection of constants, the two approaches lead to the same quantitative result in aerobic systems as the two approaches are linearly related; this can be shown to be so as follows:

Endogenous respiration formulation: (Approach 1). Let b_h be the nett endogenous respiration rate constant per day for heterotrophic organisms, then

$$dX_{a\ell}/dt = - b_h X_a \quad (\text{mg VSS}/\ell/\text{d}) \tag{8}$$

where

$X_{a\ell}$ = active organisms lost due to endogenous respiration.

A fraction, f, of the live mass that disappears is unbiodegradable and remains as endogenous residue, i.e.

$$dX_e/dt = fb_h X_a \quad (\text{mg VSS}/\ell/\text{d}) \tag{9}$$

The nett volatile mass that disappears from the system per day (mg VSS/ℓ/d) is directly equated to oxygen consumption for endogenous respiration, i,e,

$$O_e = P(1 - f)b_h X_a \ (\text{mg O}/\ell/\text{d}) \tag{10}$$

where

O_e = oxygen consumption rate for endogenous respiration (mg O/ℓ/d).

From an extensive investigation into aerobic digestion of activated sludge, Marais and Ekama (1976) concluded that, at a fixed temperature, b_h is constant and independent of sludge age - at 20°C b_h = 0,24. The value of f was found to be 0,20 and agreed with values reported in the literature (McKinney and Symons, 1964).

Death-regeneration formulation: (Approach 2). Let the actual die-off rate constant of the active organisms be b'_h per day. Let the actual unbiodegradable fraction be f'. Thus, the active mass lost ($X'_{a\ell}$) due to organism die-off is given by:

$$dX'_{a\ell}/dt = b'_h X_a \quad \text{(mg VSS/ℓ/d)} \tag{11}$$

The mass of biodegradable COD ($S'_{xa\ell}$) released back into the liquid is given by:

$$dS'_{xa\ell}/dt = P(1 - f')b'_h X_a \quad \text{(mg COD/ℓ/d)} \tag{12}$$

The mass of organisms synthesized (X'_{ag}) from this COD is given by:

$$dX'_{ag}/dt = Y_h P(1 - f')b'_h X_a \quad \text{(mg VSS/ℓ/d)} \tag{13}$$

The equivalent COD of the mass synthesized (S'_{xag}) is given by:

$$dS'_{xag}/dt = PY_h P(1 - f')b'_h X_a \quad \text{(mg COD/ℓ/d)} \tag{14}$$

The oxygen consumption associated with this synthesis of mass is the difference between Eq. (12) and Eq. (14):

$$O'_e = P(1 - f')b'_h X_a - PY_h P(1 - f')b'_h X_a$$

$$= (1 - PY_h)P(1 - f')b'_h X_a \quad \text{(mg O/ℓ/d)} \tag{15}$$

The build up of unbiodegradable cell material, X_e, is:

$$dX_e/dt = f'b'_h X_a \quad \text{(mg VSS/ℓ/d)} \tag{16}$$

Under steady state conditions, (ignoring storage of COD) both approaches must yield the same results, i.e. the endogenous residue given by Eqs. (9 and 16) must be equal. Also, in the second approach the nett mass lost is the difference between Eqs. (11 and 13) and must be equal to that given by Eq. (8). Two equations, with two unknowns, f', and b'_h are obtained:

$$fb_h = f'b'_h \tag{17}$$

$$-b_h = -b'_h + Y_h P(1 - f')b'_h \tag{18}$$

Solving for f' and b'_h in Eq. (17) and Eq. (18):

$$b'_h = \frac{(1 - Y_h Pf)}{(1 - Y_h P)} b_h \tag{19}$$

$$f' = \frac{(1 - Y_h P)}{(1 - Y_h Pf)} f \tag{20}$$

Substituting Y_h = 0,45, P = 1,48, f = 0,2 and b_h = 0,24, (after Ekama and Marais, 1978) into Eq. (19) and Eq. (20) yields b_h' = 0,62 and f' = 0,08.

The oxygen consumption for both approaches should be equal. Substituting the respective values for b_h, f, Y_h and P into Eq. (10) the oxygen consumption for endogenous respiration (Approach 1) is:

$$O_e = 0{,}285\ X_a \quad (\text{mg O}/\ell/\text{d}) \qquad (21)$$

Substituting the respective values for b_h', f', Y_h and P into Eq. (15) the oxygen utilization for cell synthesis from lysed COD (Approach 2) is:

$$O_e' = 0{,}285\ X_a \quad (\text{mg O}/\ell/\text{d})$$

The two approaches therefore yield identical results when steady state conditions are considered (storage of COD neglected). However, under dynamic conditions when all the biodegradable COD must pass through the various stages of COD adsorption, storage and finally synthesis, the second approach gives slightly different results.

Implications of the death-regeneration approach lead to some important results:

1. The actual unbiodegradable fraction of the cell is only 8 per cent instead of the usually reported value of 20 per cent. It seems that an unbiodegradable fraction for cell mass of 8 per cent seems to be more acceptable to micro-biologists than 20 per cent.

2. The actual death rate of the organisms is very high - 62 per cent of the active population disappears per day, and from the energy released through the lysis of the biodegradable cell material to the liquid phase, 39 per cent is resynthesized, resulting in a nett loss of 24 per cent per day. This implies that the bacterium's life is very short. With a death rate of 0,62 per day, 90 per cent of the organism population is replaced in 3,7 days, i.e. a half life of 1,1 days. This result is substantiated by the observation that the activity of the active organism mass remains approximately constant even at every long sludge ages, as there is continuous death and regeneration of active cells.*

The actual behaviour of the organisms is probably somewhere between the two extreme pproaches. However, this is difficult to establish as even microbiologists are uncertain of the behaviour of organisms in the "declining growth phase" (Postgate, 1976; Dawes, 1976 and Trinci and Thurston, 1976).

From a simulation study utilizing the two approaches in the mathematical model, it appears that, insofar as dynamic modelling of the aerobic activated sludge process is concerned, there is little to choose between them; nor does it appear to be of any consequence whether the energy released through the lysis of dead cell material is recirculated as readily assimilable substrate, or as slowly biodegradable

* This was determined as follows: Oxygen consumption rate tests were performed over a period of 10 days on batch samples taken from steady state activated sludge processes operated at sludge ages ranging from 2,5 to 30 days. In all the tests at a fixed temperature, the ratio of the measured oxygen consumption rates of any two consecutive days remained approximately constant. This appears to indicate that the activity of the active mass per unit of active mass remains approximately constant and is independent of sludge age (Marais and Ekama, 1976).

substrate. However, to obtain a response which correlates satisfactorily with the experimental data, it is necessary to increase the soluble substrate synthesis rate constant, K_{ms}, (Eq. 3), or to increase the particulate substrate adsorption and synthesis rate constants, K_a, and K_m, (Eqs. 1 or 2), depending on whether the energy is assumed to be soluble or slowly biodegradable. These adjustments arise in order to take into account resynthesis, or readsorption and resynthesis of the biodegradable substrate originating from the lysis of dead cell material.

The effect of the death-regeneration approach is that biodegradable substrate originating from the lysis of dead cell material is circulated through the adsorption and/or synthesis pathways, with oxygen being consumed only in the resynthesis of this substrate to active mass. This additional substrate (i.e. over and above that originating from the influent sewage) increases the load on the active organism population, which is reflected in the higher values for the kinetic constants K_a and K_m, or K_{ms} relative to their values when modelling only the nett effects as in the endogenous respiration approach.

It is possible to come to a more positive decision as to which approach, i.e. endogenous respiration or death-regeneration, is preferable when modelling the activated sludge process incorporating denitrification, i.e. by including anoxic reactors in the process configuration. When aerobically generated organisms are placed in an anoxic environment, only those capable of utilizing nitrate or nitrite as electron acceptors continue to abstract energy from the organic compounds for growth. It seems that, provided nitrate is present, the behaviour of the organisms in the anoxic environment is similar to that in an aerobic environment - the substrate utilization rate of the easily biodegrable material (K_{ms}) in an anoxic environment is approximately equal to that in an aerobic environment and the substrate utilization rate of the slowly biodegradable material in an anoxic environment is approximately 40 per cent of that in an aerobic reactor irrespective of whether the pre- or post-denitrification reactor is considered. (Van Haandel,Ekama and Marais, 1980).

When the nitrate concentration becomes effectively zero, the advantage of the death-regeneration approach to organism behaviour becomes particularly evident. Synthesis reactions cease, but organism death, with its associated lysis of biodegradable material continues, resulting in a build up of biodegradable material in the reactor. This accumulation can be considerable so that when the mixed liquor enters the aerobic reactor, in which oxygen is available as an electron acceptor, the aerobic biodegradation of the accumulation of biodegradable substrate causes a high oxygen utilization. In accordance with experimental observation (Ekama, Van Haandel and Marais, 1979) this is a rate much higher than that obtained when employing the endogenous respiration approach for with the latter, the accumulation of biodegradable substrate through cell lysis does not take place. In this respect the death-regeneration approach proves a convenient, simple and reliable framework in which to formulate the biological kinetics of the anoxic-aerobic activated sludge process.

KINETIC EQUATIONS: BI-SUBSTRATE DEATH-REGENERATION MODEL

The kinetic equations for this model are briefly listed below.

Carbonaceous Energy Removal

Influent COD fractions. The following influent COD fractions are recognized:

$$S_{ti} = S_{bi} + S_{ui} + S_{pi} \qquad (23)$$

where

S_{ti} = total influent COD concentration (mg COD/ℓ)
S_{bi} = total biodegradable COD concentration (mg COD/ℓ)
S_{ui} = soluble unbiodegradable COD concentration (mg COD/ℓ)
S_{pi} = particulate unbiodegradable COD concentration (mg COD/ℓ).

In accordance with the bi-substrate hypothesis the biodegradable COD concentration is divided into two fractions, i.e.

$$S_{bi} = S_{bsi} + S_{bpi} \tag{24}$$

where

S_{bsi} = readily assimilable biodegradable COD concentration (mg COD/ℓ)
S_{bpi} = slowly biodegradable particulate COD concentration (mg COD/ℓ).

It is convenient to express these concentrations as fractions of the total influent COD concentration, i.e.

$$S_{pi} = f_{up}S_{ti} \tag{25}$$

$$S_{ui} = f_{us}S_{ti} \tag{26}$$

$$S_{bi} = S_{ti}(1 - f_{us} - f_{up}) \tag{27}$$

$$S_{bsi} = f_{bs}S_{bi} \tag{28}$$

$$S_{bpi} = (1 - f_{bs})S_{bi} \tag{29}$$

where

f_{up} = particulate unbiodegradable COD fraction
f_{us} = soluble unbiodegradable COD fraction
f_{bs} = readily assimilable biodegradable COD fraction.

Adsorption of particulate biodegradable COD. The Blackwell (1971) formulation, as modified by Ekama and Marais (1979), defines the rate of particulate biodegradable adsorption as:

$$dS_{bp\ell}/dt = - K_a S_{bp} X_a (f_{ma} - X_s/X_a) \tag{30}$$

where subscript ℓ refers to the concentration decrease.

Hence the rate of increase of stored COD is given by:

$$dX_{sg}/dt = + K_a S_{bp} X_a (f_{ma} - X_s/X_a)/P \tag{31}$$

where subscript g refers to the concentration increase.

The adsorption rate constant, K_a, changes with temperature according to the following equation:

$$K_{aT} = K_{a20}(1{,}029)^{(T-20)} \tag{32}$$

where subscripts T and 20 refer to temperature T and 20°C respectively.

Synthesis of cell mass. The synthesis of active mass from readily assimilable biodegradable COD is modelled by the Monod relationship, i.e.

$$\frac{dX_{ag}}{dt} = Y_h\left[\frac{K_{ms}S_{bs}}{K_{ss} + S_{bs}}\right]X_a \tag{33}$$

where

K_{ms} = maximum specific growth constant utilizing soluble substrate (mg COD/(mg COD/mg VSS/d)

K_{ss} = half-saturation coefficient for soluble substrate (mg COD/ℓ).

Hence the utilization of S_{bs} is given by:

$$\frac{dS_{bs\ell}}{dt} = -\left[\frac{K_{ms}S_{bs}}{K_{ss} + S_{bs}}\right]X_a \tag{34}$$

and the oxygen consumption rate for the utilization of S_{bs} is

$$O_{ss} = (1 - PY_h)\left[\frac{K_{ms}S_{bs}}{K_{ss} + S_{bs}}\right]X_a \tag{35}$$

The synthesis of active mass from stored COD is given by Eq. (8), i.e.

$$\frac{dX_{ag}}{dt} = Y_h\left[\frac{K'_{mp}X_sP}{K'_{sp}X_a + X_sP}\right]X_a \tag{36}$$

where

K'_{mp} = maximum specific growth rate constant for the utilization of stored COD (mg COD/mg VSS/d)

K'_{sp} = half-saturation coefficient for the utilization of stored COD (mg COD/mg VSS).

The overall rate of change of stored COD is given by the difference between Eqs. (31 and 36), i.e.

$$\frac{dX_a}{dt} = K_sS_{bp}X_a(f_{ma} - \frac{X_s}{X_a})/P - \left[\frac{K'_{mp}X_s}{K'_{sp}X_a + X_sP}\right]X_a \tag{37}$$

The utilization of stored COD is given by:

$$\frac{dX_{s\ell}}{dt} = -\left[\frac{K'_{mp}X_s}{K'_{sp}X_a + X_sP}\right]X_a \tag{38}$$

and the oxygen consumption rate for synthesis from stored COD is given by:

$$O_{sp} = (1 - PY_h)\left[\frac{K'_{mp}X_sP}{K'_{sp}X_a + X_sP}\right]X_a \quad (39)$$

Hence the total carbonaceous oxygen consumption rate is the sum of Eqs. (35 and 39), i.e.

$$O_c = (1 - PY_h)\left[\frac{K_{ms}S_{bs}}{K_{ss} + S_{bs}} + \frac{K'_{mp}X_sP}{K'_{sp}X_a + X_sP}\right]X_a \quad (40)$$

and the overall synthesis of active mass is the sum of Eqs. (33 and 36), i.e.

$$\frac{dX_{ag}}{dt} = Y_h\left[\frac{K_{ms}S_{bs}}{K_{ss} + S_{bs}} + \frac{K'_{mp}X_sP}{K'_{sp}X_a + X_sP}\right]X_a \quad (41)$$

The temperature dependency of the growth kinetic constants have been found to vary in accordance with the following equations:

$$K_{msT} = K_{ms20}(1{,}200)^{(T-20)} \quad (42)$$

$$K_{ssT} = K_{ss20}(1{,}000)^{(T-20)} \quad (43)$$

$$K'_{mpT} = K'_{mp20}(1{,}029)^{(T-20)} \quad (44)$$

$$K'_{spT} = K'_{sp20}(1{,}100)^{(20-T)} \quad (45)$$

Cell death. The loss of active mass due to organism death is given by Eq. (11). Hence the overall rate of change of active mass is found by combining Eqs. (41 and 11), i.e.

$$\frac{dX_a}{dt} = Y_h\left[\frac{K_{ms}S_{bs}}{K_{ss} + S_{bs}} + \frac{K'_{mp}X_sP}{K'_{sp}X_a + X_sP}\right]X_a - b'_hX_a \quad (46)$$

The concentration of biodegradable COD released back to the liquid phase due to organism death is given by Eq. (12) and is considered to be slowly biodegradable COD. Combining Eqs. (30 and 32), the overall rate of change of slowly biodegrable COD is given by:

$$dS_{bp}/dt = -K_aS_{bp}X_a(f_{ma} - X_s/X_a) + P(1 - f')b'_hX_a \quad (47)$$

Nitrification

The formulation of the kinetics of biological nitrification as proposed by Ekama and Marais (1979) is accepted without modification. A summary of the pertinent equations is given below:

Influent TKN fractions. The total influent TKN is divided into the following fractions:

$$N_{ti} = N_{ai} + N_{oi} + N_{ui} + N_{pi} \quad (48)$$

where

N_{ti} = total influent TKN concentration (mg N/ℓ)

N_{ai} = influent free and saline ammonia concentration (mg N/ℓ)

N_{ui} = influent soluble unbiodegradable TKN concentration (mg N/ℓ)

N_{pi} = influent particulate unbiodegradable TKN concentration.

It is convenient to express these concentrations as fractions of the total influent TKN concentration, i.e.

$$N_{ai} = f_{na}N_{ti} \tag{49}$$

$$N_{ui} = f_{nu}N_{ti} \tag{50}$$

$$N_{pi} = f_{n}S_{ti}/P \tag{51}$$

$$N_{oi} = N_{ti} - N_{ai} - N_{ui} - N_{pi}$$

$$= (1 - f_{na} - f_{nu} - S_{ti}/N_{ti}\cdot f_{n}/P)N_{ti} \tag{52}$$

where

f_{na} = influent ammonia fraction

f_{nu} = soluble unbiodegradable TKN fraction

f_{n} = TKN/VSS ratio.

The nitrification kinetics are based on the assumption that the behaviour of *nitrosomonas* governs the behaviour of nitrification in the activated sludge process. The specific growth of these nitrifiers is modelled with a Monod relationship. i.e.

$$\mu_{n} = \mu_{nm}N_{a}/(K_{n} + N_{a}) \tag{53}$$

where

μ_{n} = specific growth rate of *nitrosomonas*

μ_{nm} = maximum specific growth rate of *nitrosomonas* (/d)

K_{n} = half-saturation coefficient for the utilization of ammonia (mg N/ℓ)

N_{a} = ammonia concentration (mg N/ℓ).

The nett growth rate of the nitrifiers is given by

$$\frac{dX_{n}}{dt} = \left[\frac{\mu_{nm}N_{a}}{K_{n} + N_{a}}\right]X_{n} - b_{n}X_{n} \tag{54}$$

where

X_{n} = concentration of nitrifiers (mg VSS/ℓ)

b_{n} = endogenous respiration rate of the nitrifiers (/d)

The rate of conversion of ammonia to nitrate follows from Eq. (53) i.e.

$$\frac{dN_{a}}{dt} = \left[\frac{(\mu_{nm}/Y_{n})N_{a}}{K_{n} + N_{a}}\right]X_{n} \tag{55}$$

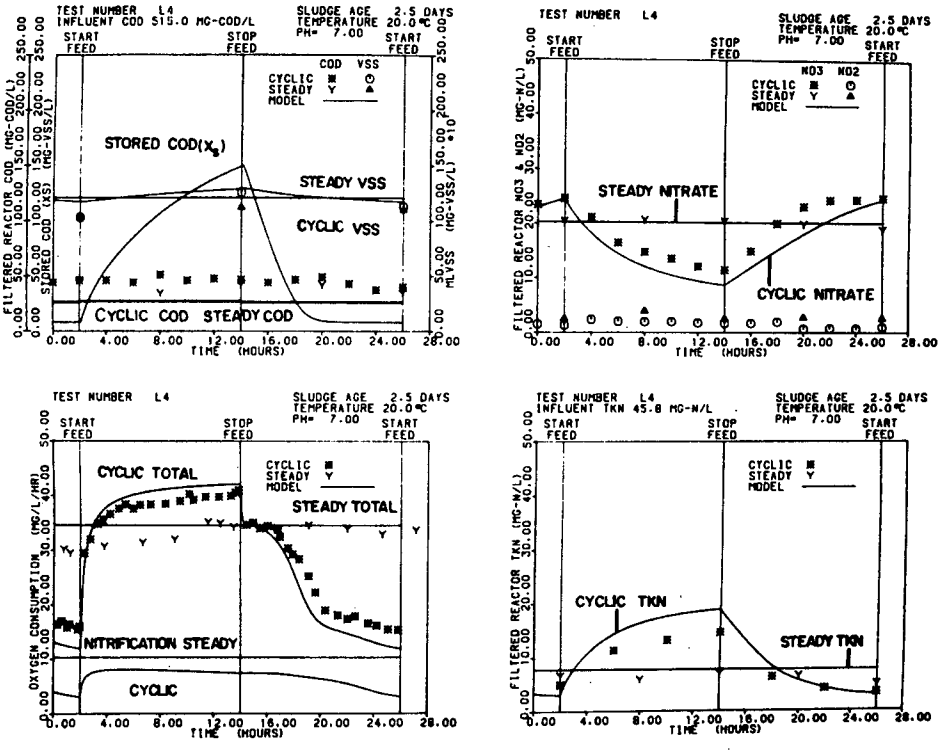

Fig. 3. Comparison of the response waves predicted by the theoretical model with those observed experimentally under daily cyclic square wave loading conditions at 2,5 days sludge age, pH 7,0 and temperature 20°C. (Test No. L4).

where

Y_n = yield coefficient for the nitrifiers (mg VSS/mg N).

As the mass of nitrogen incorporated into the nitrifiers for synthesis is negligible, (Haug and McCarty, 1971), it is assumed that the conversion of ammonia to nitrate is stoichiometric, hence:

$$\frac{dN_n}{dt} = +\left[\frac{(\mu_{nm}/Y_n)N_a}{K_n + N_a}\right] X_n \qquad (56)$$

where

N_n = nitrate concentration (mg N/ℓ)

and the oxygen consumption rate for nitrification is:

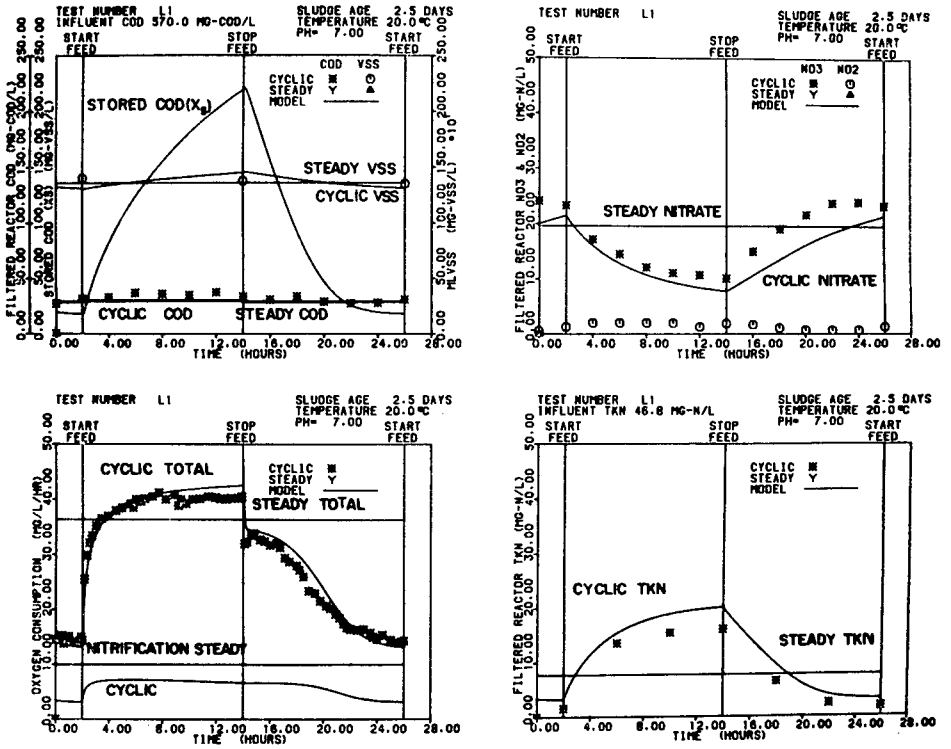

Fig. 4. Comparison of the response waves predicted by the theoretical model with those observed experimentally under daily cyclic square wave loading conditions at 2,5 days sludge age, pH 7,0 and temperature 20°C. (Test No. L1.)

$$O_n = 4{,}57\left[\frac{(\mu_{nm}/Y_n)N_a}{K_n + N_a}\right] X_n \qquad (57)$$

where

O_n = oxygen consumption rate for nitrification (mg O/ℓ/d).

Heterotrophic organisms convert organic nitrogen to ammonia in accordance with a first order rate with respect to the organic nitrogen and the active mass concentrations, i.e.

$$dN_o/dt = - K_r N_o X_a \qquad (58)$$

where

K_r = organic nitrogen conversion rate (ℓ/mg VSS/d).

The kinetic constants μ_{nm}, K_n, b_n, Y_n and K_r vary with temperature and mixed liquor pH in accordance with the following equations:

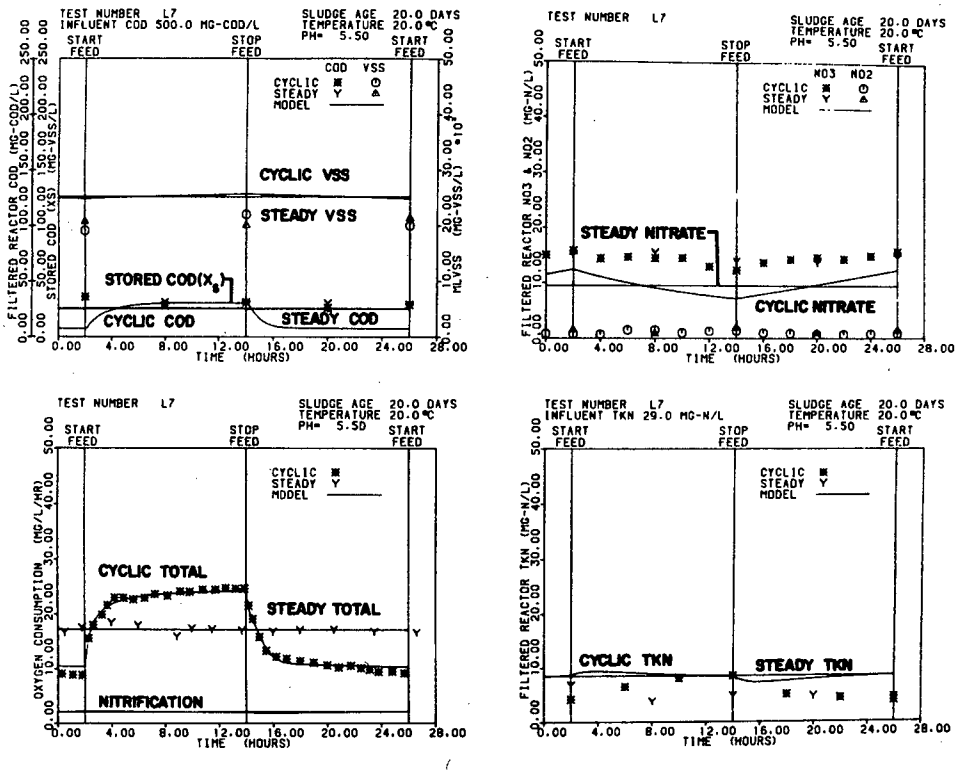

Fig. 5. Comparison of the response waves predicted by the theoretical model with those observed experimentally under daily cyclic square wave loading conditions at 20 days sludge age, pH 5,5 and temperature 20°C.

$$\mu_{nmTp} = \mu_{nm}(1,123)^{(T-20)}(2,350)^{(p-7,20)} \quad (59)$$

$$K_{nTp} = K_n(1,123)^{(T-20)}(2,350)^{(7,20-p)} \quad (60)$$

$$b_{nTp} = b_n(1,029)^{(T-20)}(1,000)^{(p-7,20)} \quad (61)$$

$$Y_{nTp} = Y_n(1,000)^{(T-20)}(1,000)^{(p-7,20)} \quad (62)$$

$$K_{rTp} = K_r(1,029)^{(T-20)}(1,000)^{(p-7,20)} \quad (63)$$

where subscripts T and p refer to temperature in °C and mixed liquor pH respectively. Mixed liquor pH values between 7,2 and 8,5 do not affect the kinetic constants, i.e. when p > 7,2, 2,350 becomes 1,000.

VERIFICATION OF THE MODEL

Verification of the activated sludge model proceeded in two stages: (1) calibration, in order to evaluate some of the kinetic constants, and (2) application of

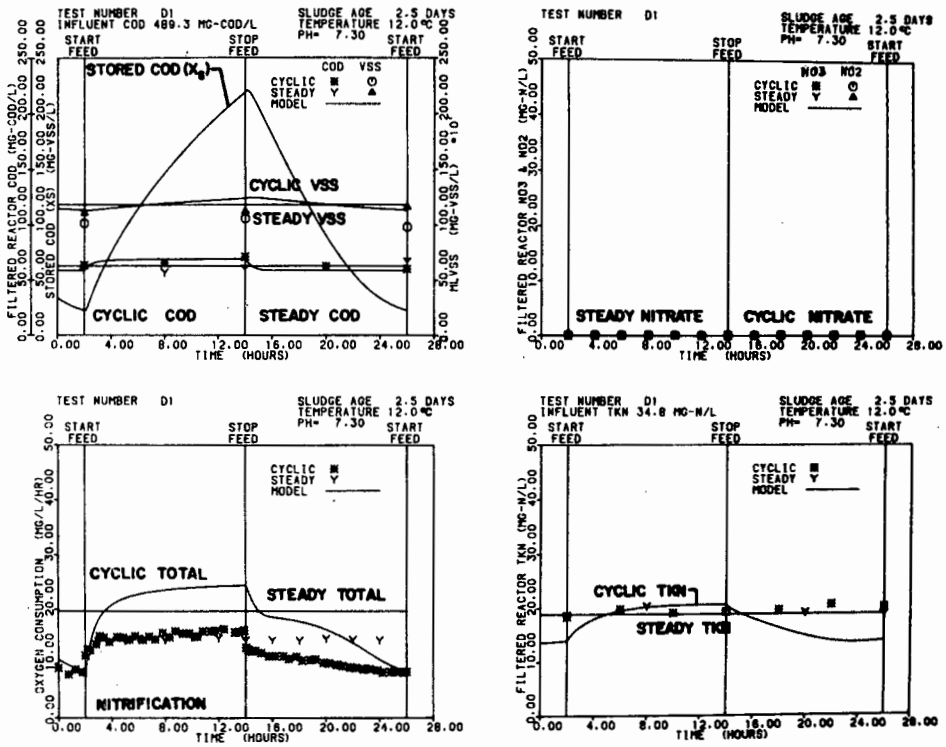

Fig. 6. Comparison of the response waves predicted by the theoretical model with those observed experimentally under daily cyclic square wave loading conditions at 2,5 days sludge age, pH 7,3 and temperature 12°C. (COD/VSS ratio = 1,48).

of the model to a range of process configurations under different conditions to test its validity and assess its limitations.

To calibrate the model the time dependent - spatially independent system, the single reactor activated sludge process, was chosen because it is a simple system, yet flexible in the variety of different conditions that can be imposed on it. Daily cyclic loading conditions were obtained by imposing a square wave (12 hours on, 12 hours off) influent flow on the system. By using a square wave, the dynamic response of the system is effectively brought into prominence. The influence of sludge age was obtained by conducting sets of tests at 2,5 and 20 day sludge ages, respectively. Temperature dependency was obtained by running the series of tests at 12°C and 20°C.

To determine the range of validity of the calibrated model, the model was tested on two systems: (1) on time-independent and space-dependent systems: experimental data was obtained at laboratory scale on a series reactor system under constant flow conditions; and (2) on time- and space-dependent systems experimental data was obtained at pilot scale on a series reactor system under cycling loading

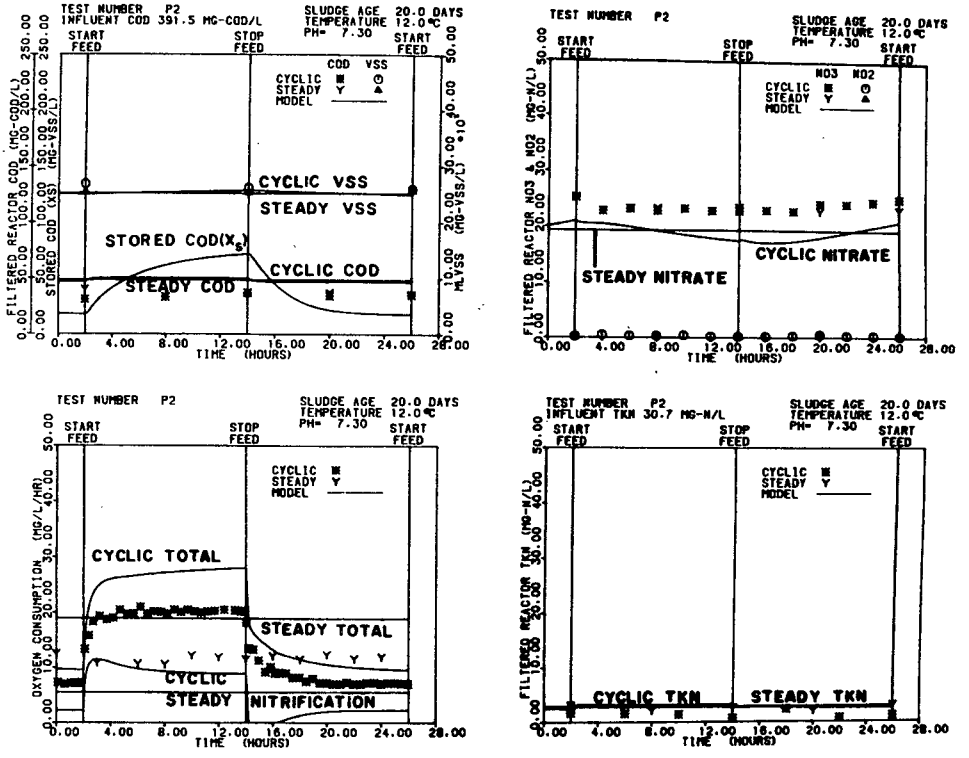

Fig. 7. Comparison of the response waves predicted by the theoretical model with those observed experimentally under daily cyclic square wave loading conditions at 20 days sludge age, pH 7,3 and temperature 12°C. (COD/VSS ratio = 1,48).

conditions - the influent was drawn from a main sewer at constant rate, with the average COD exhibiting the diurnal variation normally encountered in domestic flows.

All the laboratory scale units were operated with unsettled sewage obtained from one of the main sewer outfalls in Cape Town. This wastewater was mainly of domestic origin, having a low alkalinity and low calcium content. The pilot scale plant was operated with settled sewage from a large treatment works in Pretoria. This wastewater had an appreciable industrial content, a high alkalinity and a high calcium content. The two waste flows therefore, differed appreciably and served a useful purpose in testing the model for different wastewater compositions. Details of the various experimental studies have been fully documented (Ekama and Marais, 1978).

The calibration of the model proceeded by trial and error, by assigning values to the kinetic constants for which no values were available from other sources. The values finally assigned are listed in Table 1, together with other constants utilized in the model. These values are averages that gave the best mean correspondence between the predicted and experimental data for the complete set of experiments.

TABLE 1 Values of Kinetic and Other Constants used in the Model for the Activated Sludge (see Appendix for nomenclature)

Symbol	Value	Units	Symbol	Value	Units
Carbonaceous Material Degradation Kinetics					
K_{a20}	0,250	ℓ/mg VSS.d	K_{r20}	0,023	ℓ/mg VSS.d
K_{ms20}	8,00	mg VSS/mg COD	f_{oe}	0,00	mg N/mg VSS
K_{ss20}	20,0	mg COD/ℓ	f_{os}	1,00	mg N/mg VSS
K'_{mp20}	3,00	mg COD/mg VSS.d	θ_{ha}	1,029	
K'_{sp20}	0,04	mg COD/mg VSS		1,200 for K_{ms}	
b'_{h20}	0,62	d^{-1}	θ_{hs}	1,000 for K_{ss} 1,029 for K'_{mp}	
Y_h	0,45	mg VSS/mg COD		$1,100^{-1}$ for K'_{sp}	
f'	0,08	mg VSS/mg VSS			
f_n	0,10	mg N/mg VSS	θ_{he}	1,029	
P	1,48	mg COD/mg VSS	ϕ_{ha}	1,000	
f_{ma}	1,00	mg VSS/mg VSS	ϕ_{hs}	1,000	
f_{bs}	0,24	mg COD/mg COD	ϕ_{he}	1,000	
Nitrification Kinetics					
μ_{nm20}*	0,65 0,21	d^{-1}	b_{n20}	0,04	d^{-1}
K_{n20}	1,00	mg N/ℓ	Y_n	0,10	mg VSS/mg N
θ_{ns}	1,123		ϕ_{ns}	2,350	
θ_{ne}	1,029		ϕ_{ne}	1,000	
Influent Wastewater Fractions					
f_{us}*	0,033 0,050	mg COD/mg COD	f_{un}*	0,00 0,00	mg N/mg N
f_{up}*	0,025 0,090	mg VSS/mg COD	f_{sn}*	0,84 0,75	mg N/mg N

* Upper value refers to unsettled wastewater; lower value to settled wastewater.

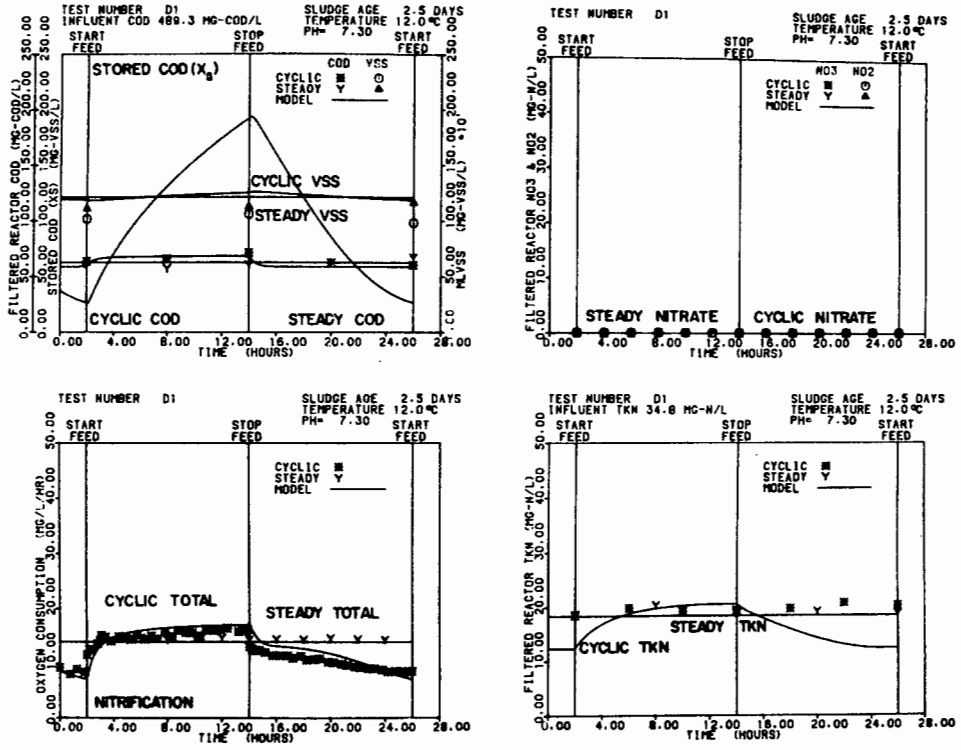

Fig. 8. Comparison of the response waves predicted by the theoretical model with those observed experimentally under daily cyclic square wave loading conditions at 2,5 days sludge age, pH 7,3 and temperature 12°C. (COD/VSS ratio = 1,72).

The responses of the different process variables observed experimentally and that predicted by the model for two 24 hour cycles and a 2,5 day sludge age and one 24 hour cycle at a 20 day sludge age, both at 20°C, are shown in Figs. 3, 4 and 5, respectively.

Temperature effects were evaluated by modifying the kinetic constants obtained at 20°C to fit the data observed at 12°C. The results of this endeavour, for two such tests, are shown in Figs. 6 and 7. It can be noted that a good fit could not be obtained at either a 2,5 day or 20 day sludge age. The shape of the predicted oxygen utilization rate response for both tests appears to be approximately correct, but the values are generally over-predicted. After an extensive investigation it was concluded that this was due to the effect of parameters other than the kinetic constants. Attention was directed to the COD/VSS ratio.

Several theoretical COD/VSS ratios have been reported in the literature, all based on empirical stoichiometric formulations for microbial sludge. These theoretical values fall in the range of 1,22 to 1,48 mg COD/mg VSS. Marais and Ekama (1976) conducted an extensive series of tests on raw sewage, activated sludge MLVSS and

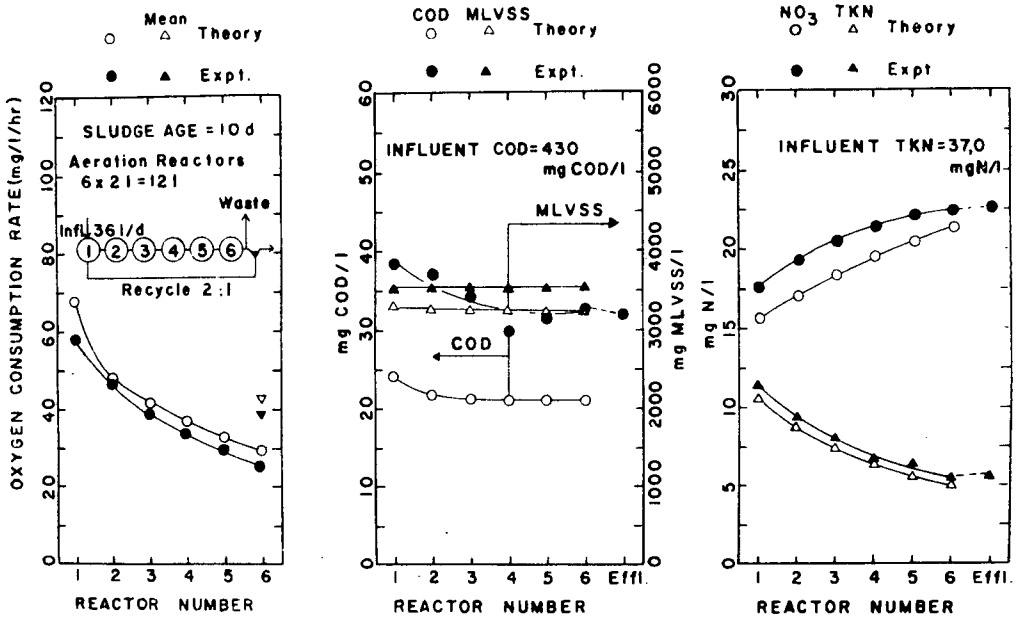

Fig. 9. Comparison of process variable response profiles predicted by the theoretical model with those observed experimentally in a series reactor process under constant loading conditions at 10 days sludge age, pH 6,05 and 20°C.

aerobically digested activated sludge. The mean value of their experimentally determined values fell in the range 1,43 to 1,48 mg COD/VSS. Now the equivalence of VSS and COD allows an energy balance, in terms of COD, to be made between energy utilized, sludge synthesized and oxygen consumed during the synthesis reaction.

Such mass balances form the basis for the assessment of the validity of experimental data. Experiments conducted at 20°C generally gave COD mass retrievals of greater than 95 per cent when using a COD/VSS ratio of 1,48. However, experiments conducted at 12°C exhibited a COD mass retrieval of about 85 per cent when using this value of 1,48. This observation led to the initiation of an investigation into the possible variation of the value of the COD/VSS ratio with temperature and process parameters such as sludge age. Simultaneous determination of the COD/VSS ratio of activated sludge MLVSS from laboratory units operated at 20°C and 12°C treating sewage from the same source, showed significantly different values (see Table 2).

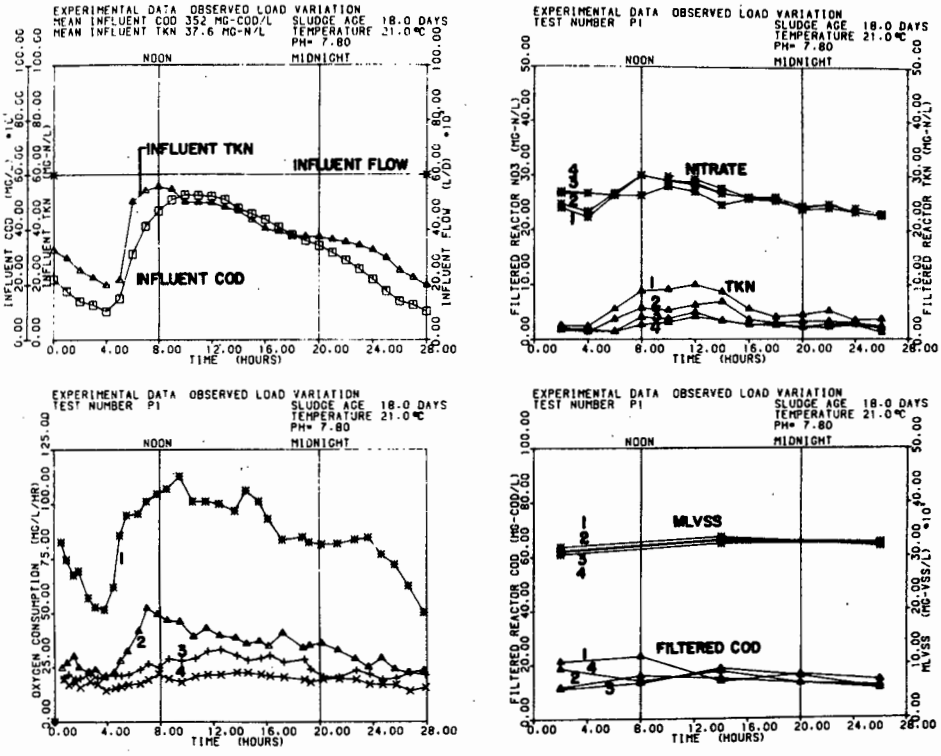

Fig. 10. Experimental process variable response waves observed in the series reactor pilot plant under cyclic loading conditions at 18 days sludge age, pH 7,8 and temperature 21°C.

TABLE 2 COD/VSS ratios for Mixed Liquor in Laboratory Scale Activated Sludge Units.

Sludge age	Temperature	
	20°C	12°C
2,5	1,50	1,72
20	1,55	1,69

Using these constants in the respective 24 hour test data, average mass balances on COD of 95 per cent and better were obtained at 12°C.

Of greater significance was that, using these experimentally determined COD/VSS ratios, a good correspondence between experimentally observed and predicted oxygen utilization rates at both 2,5 and 20 day sludge ages at 12°C was obtained (Fig. 8 - cf Fig. 6).

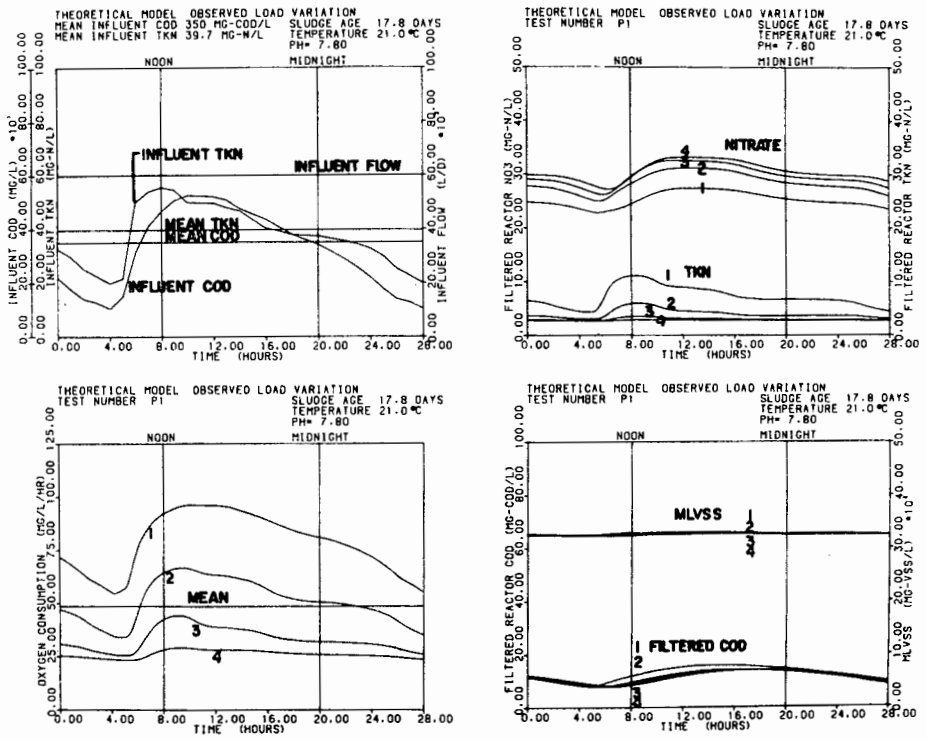

Fig. 11. Theoretical process variable response waves predicted for the series reactor plant under cyclic loading conditions at 18 days sludge age, pH 7,8 and 21°C.

In the bi-substrate hypothesis there is some uncertainty as to the values ascribed to the maximum specific substrate utilization rate constant for soluble substrate, K_{ms}, and the associated half-saturation coefficient, K_{ss}. For the aerobic activated sludge process values of 8 mg COD/mg VSS/d and 20 mg COD/ℓ for K_{ms} and K_{ss}, respectively, result in a soluble substrate utilization rate fast enough to predict a precipitous drop in the oxygen utilization rate observed in Figs. 3 and 4.

To simulate the cyclic response of the filtered COD concentration observed in the contact reactor of the contact stabilization modification of the CMAS process, Alexander, Ekama and Marais (1980) found that the value of K_{ms} had to be reduced from 8 to 2 mg COD/mg VSS/d. The need for this change indicates a possible deficiency in the model.

It was stated above that the range of the validity of the model (developed on time-dependent space-independent systems) was assessed by comparing predicted and experimental responses on both time-independent space-dependent and time- and space-dependent configurations. For verification under time-independent space-dependent conditions, a set of laboratory experiments was conducted on a process configuration consisting of six completely mixed reactors in series under constant

flow and load conditions at a 10 day sludge age and 20°C. The experimental results are shown in Fig. 9. The theoretical response was simulated, without changing any of the constants developed in calibrating the model (Table 1). The simulated data are also plotted in Fig. 9. It can be seen that there is excellent correspondence.

For verification under time- and space-dependent conditions, experiments were done at pilot scale. The pilot plant (situated at Pretoria) consisted of four 5 m^3 aeration reactors in series. A constant flow of 60 m^3 /d settled wastewater was imposed on the pilot plant but a cyclic load resulted from the diurnal variation in influent COD and TKN concentrations. The pilot plant was operated at an 18 day sludge age and a sludge recycle ratio of 2:1 at approximately 21°C. The experimental data, including the influent COD and TKN concentrations, observed over a 24 hour cycle are shown in Fig. 10. The input data were used in a simulation study with the kinetic and other constants for settled wastewater listed in Table 1. The theoretical model response is shown in Fig. 11.

To obtain the good correlation between experimental and predicted data, a value of the maximum specific growth rate of the *nitrosomonas*, μ_{nm}, of 0,21 d^{-1} had to be accepted - a value three times lower than that for Cape Town wastewater (Table 1). Such a decrease is not unjustified; Pretoria wastewater contains an appreciable industrial fraction, whereas the wastewater of Cape Town is principally from domestic sources and is less toxic towards nitrifiers. Generally, μ_{nm} is very sensitive to any inhibitory substances. During any series of experiments utilizing the same sewage source, it is not uncommon to find variation of μ_{nm} from one batch of sewage to another. A range of μ_{nm} from 0,2 to 0,65 for different waste flows is therefore not unexpected.

CLOSURE

The general model utilizing the biological mechanisms proposed in this paper satisfactorily predicts the behaviour of the activated sludge process operating over a range of process configurations under constant and cyclic loading conditions. In particular, it should be noted that this was found possible without changing the values of kinetic constants of the model under the different operating and loading conditions.

Application of the general model to predict the dynamic behaviour of the single sludge denitrification process (van Haandel, Ekama and Marais, 1980) had indicated that different values of the kinetic constants defining the carbonaceous and ammoniacal substrate utilization rates are required for the anoxic reactor of the system. However, such changes are to be expected as the final electron acceptor in the anoxic reactor is nitrate instead of oxygen.

Application of the general model to the contact stabilization process (Alexander, Ekama and Marais, 1980) has indicated that a reduction in the maximum soluble substrate utilization rate at 20°C (K_{ms20}) from 8,0 to 2,0 mg COD/mg VSS/d is necessary to satisfactorily simulate the behaviour of the process under constant and cyclic conditions of loading.

The need for this change in K_{ms20} is of a more serious nature than the changes required for describing anoxic conditions, because the contact stabilisation process is completely aerobic. This indicates a deficiency in the basic mechanism of the general model. However, once the revised values of the kinetic constants for the anoxic reactor and the contact stabilization process are accepted, the model satisfactorily simulated the behaviour of these systems under constant and cyclic loading conditions.

This paper discussed only the basic biological mechanisms and their kinetics as hypothesized by the authors. The process equations are not presented as these can be readily developed (by considering mass balance and continuity principles of each process variable over each component of the configuration) once the biological mechanisms are known.

The biological mechanisms proposed by the authors are unlikely to be final and should be regarded only as an advance in understanding biological behaviour insofar as the activated sludge process is concerned.

ACKNOWLEDGEMENT

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LIST OF SYMBOLS

b^* = general parameter for endogenous respiration rate, d^{-1}. Subscripts h or n refer to heterotrophic or nitrifying organisms, respectively. Values marked ' refer to the death-regeneration hypothesis

f = unbiodegradable fraction of the active mass, mg VSS/mg VSS

f_{bs} = fraction of biodegradable substrate (COD) which is soluble, mg COD/mg COD

f_{ma} = maximum fraction of substrate (as VSS) that can be incorporated in the active volatile sludge mass, mg VSS/mg VSS

f_n = nitrogen fraction of the sludge, mg N/mg VSS

f_{oe} = organic nitrogen fraction of the nitrogen released by active heterotrophic organism death, mg N/mg N

f_{os} = organic nitrogen fraction of the nitrogen required for heterotrophic cell synthesis, mg N/mg N

f_{sn} = free and saline ammonia fraction of the influent TKN, mg N/mg N

f_{un} = soluble unbiodegradable fraction of the influent TKN, mg N/mg N

f_{up} = particulate unbiodegradable fraction of the influent COD, mg VSS/mg COD

f_{us} = soluble unbiodegradable fraction of the influent COD, mg COD/mg COD

K_a^* = particulate substrate adsorption rate constant, ℓ/mg VSS.d

K_m^* = maximum specific substrate utilization rate constant for stored substrate (as mg COD) for Ekama and Marais (1978) theory, mg COD/mg VSS.d

K'^*_{mp} = maximum specific substrate utilization rate constant for stored substrate (as COD) based on the adsorption site approach, mg COD/mg VSS.d

K_{ms}^* = maximum specific substrate utilization rate constant for soluble substrate, mg COD/mg VSS.d

K_n*† = saturation coefficient for nitrification, mg N/ℓ

K_r* = conversion rate of organic nitrogen to free and saline ammonia, ℓ/mg VSS.d

K_s* = half saturation coefficient for heterotrophic cell synthesis for stored substrate (as mg COD) for Ekama and Marais (1978) theory, mg COD/ℓ

K'_{sp}* = half-saturation coefficient for heterotrophic cell synthesis for stored substrate (as mg COD) based on the adsorption site approach, mg COD/mg VSS

K_{ss}* = half-saturation coefficient for heterotrophic cell synthesis for soluble substrate, mg COD/ℓ

N = general parameter for nitrogen concentration, mg N/ℓ. Subscripts a, n, o, t and u refer to ammonia, nitrate, organic nitrogen, TKN, and unbiodegradable concentrations, respectively

n = factor for adsorption site theory depending on the volume to surface ratio for the active mass

O = general parameter for oxygen consumption rate, mg O/ℓ/d. Subscripts a, c, e, n, s, and t refer to adsorption, carbonaceous, endogenous respiration, nitrification, synthesis, and total fractions, respectively

P = COD : VSS ratio, mg COD/mg VSS

S = general parameter for substrate (COD) concentrations, mg COD/ℓ. Subscripts b, u, and t refer to biodegradable, unbiodegradable soluble, and total fractions, respectively

t = Time (d)

X = general parameter for sludge concentration (mg VSS/ℓ). Subscripts a, e, n, s, and v refer to active, endogenous, nitrifier, stored, and total volatile concentrations, respectively. Additional subscripts g or ℓ refer to concentrations gained or lost as a result of process reaction

Y_h = heterotrophic organism yield coefficient in terms of substrate as COD, mg VSS/mg COD

Y_n = nitrifying organism yield coefficient, mg VSS/mg N

μ*† = general parameter for *specific* growth rate, d^{-1}. Subscripts h or n refer to heterotrophic or nitrifying organisms, respectively. Additional subscript m refers to maximum value

θ = general Arrhenius parameter for the temperature dependency coefficient. Subscripts h and n refer to heterotrophic and nitrifying organisms, respectively. Additional subscripts a, e, and s refer to adsorption, endogenous respiration, and synthesis values, respectively

ϕ = general Arrhenius parameter for the pH dependency coefficient. Subscripts h and n refer to heterotrophic and nitrifying organisms, respectively. Additional subscripts a, e and s refer to adsorption, endogenous respiration, and synthesis values, respectively.

* Additional subscripts T or 20 refer to the value at T or 20°C respectively.

† Additional subscripts p or 7,2 refer to the value at pH equal to p or 7,2 respectively.

REFERENCES

Alexander, W.V., G.A.Ekama and G.v.R.Marais (1980). The activated sludge process Part 3 - application of the general kinetic model to the contact stabilization process. Presented at this Conference.

Blackwell, L.G. (1971). A theoretical and experimental evaluation of the transient response of the activated sludge process. Ph.D. thesis, Clemson Univ., Clemson, S.Carolina.

Busby, J.L. and J.F.Andrews (1973). Dynamic modelling and control strategies for the activated sludge process. Res.Rept., Dept. of Environ. Systems Eng., Clemson Univ., Clemson, S.Carolina.

Dawes, E.Q. (1976). Endogenous metabolism and the survival of starved prokaryates. In T.R.C.Gray and J.R.Postgate (Eds.) The Survival of Vegetative Microbes, 26th Symposium of the Society of General Microbiology, Univ. of Cambridge, Cambridge, University Press, Cambridge.

Downing,A.L., H.A.Painter and G.Knowles (1964). Nitrification in the activated sludge process. J.Proc.Inst.Sew.Purif., 64, 130-158

Ekama, G.A. and G.v.R.Marais (1978). The dynamic behaviour of the activated sludge process. Res.Rept. No. W.27, Dept. of Civil Eng., Univ. of Cape Town.

Ekama, G.A. and G.v.R.Marais (1979). Dynamic behaviour of the activated sludge process, Jour.Water Poll.Control Fed., 51, 534-556.

Ekama, G.A., A.C.van Haandel and G.v.R.Marais (1979). The present status of research on nitrogen removal: a model for the modified activated sludge process. Presented at: Symposium on Nutrient Removal, Council for Scientific and Industrial Research, 17th May, 1979. To be published in Water S.A.

Ford, D.L. and W.W.Eckenfelder,Jr. (1967). The rôle of enzymes in the contact stabilization process - discussion. Advances in Water Pollution Research,2. Article by R.H.Siddinqi, R.S.Engelbrecht and R.E.Speece (1967). Jour.Water Poll.Control Fed., 39, 1211-1222.

Gaudy, A.F. Jr., O. Obayashi and E.T.Gaudy (1971). Control of growth rate by initial substrate concentration at values below maximum rate. Appl.Microbiol. 22, 1041-1047.

Haug, T.R. and P.L.McCarty (1971). Nitrification with the submerged filter. Presented at 44th Am.Conf.Water Poll.Control Fed., 1971.

Jacquart, J.C., D.Lefort and J.M.Lovel (1973). An attempt to take account of biological storage in the mathematical analysis of activated sludge behaviour. In S.H.Jenkins (Ed.) Advances in Water Pollution Research, Pergamon Press, New York.

Lawrence, A.W. and P.L.McCarty (1970). Unified Basis for biological treatment design and operation. J.San.Eng.Div., ASCE, 96, SA3, 757, 778.

Levenspiel, O. (1972). Chemical Reaction Engineering, 2nd Ed., John Wiley, New York, pp. 465-469.

Marais, G.v.R. and G.A.Ekama (1976). The activated sludge process Part 1 - steady state behaviour. Water S.A., 2, 4, 163.

McKinney, R.E. (1962). Mathematics of complete mixing activated sludge. J.San. Eng.Div., ASCE, 88, SA3, Proc. Paper 3133, 87.

McKinney, R.E. and J.M.Symons (1964). Growth and endogenous metabolism: a discussion. Proc. 1st Inter.Conf. on Water Pollution Control, London, 1962, Pergamon Press, Oxford.

Monod, J. (1950). Technique of continuous culture - theory and application. Ann.Inst.Pasteur, 79, 167.

Morris, J.C. and W.Stumm (1960). Colloidal aspects of waste treatment. Proc. Rudolphs Research Conf., Rutgers Univ., June, 1960.

Porges,N., L.Jasewicz and S.R.Hoover (1956). Principles of biological oxidations. In B.J.McCabe and W.W.Eckenfelder,Jr. (Eds.) Biological Treatment of Sewage and Industrial Wastes, Vol. 1, Reinhold Publ.Co., New York, pp. 35-48.

Postgate, J.P. (1976). Death in Microbes and Macrobes. In T.R.G.Gray and J.R. Postgate (Eds.) The Survival of Vegetative Microbes, 26th Symposium of the Society of General Microbiology, Univ. of Cambridge, Cambridge Univ. Press, Cambridge.

Stenstrom, M.K. (1975). A dynamic model and computer compatible control strategies for wastewater treatment plants. Ph.D. thesis, Clemson Univ., Clemson, S.Carolina.

Trinci, A.P.J. and C.F.Thurston (1976). Transition to the non-growing stage in eukaryatic micro-organisms. In T.R.G.Gray and J.R.Postgate (Eds.) The Survival of Vegetative Microbes, 26th Symposium of the Society of General Microbiology, Univ. of Cambridge, Cambridge Univ. Press, Cambridge.

Wilson, D.E. and G.v.R.Marais (1976). Adsorption phase in biological denitrification. Res.Rept. No. W.11, Dept. of Civil Eng., Univ. of Cape Town.

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THE ACTIVATED SLUDGE PROCESS PART 2. APPLICATION OF THE GENERAL KINETIC MODEL TO THE CONTACT STABILIZATION PROCESS

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Abstract—The general aerobic activated sludge model including nitrification for processes treating principally municipal wastewater is applied to the contact stabilization process treating municipal wastewaters. The application involves two changes to the model: (i) a change in one of the values of the kinetic constants in the expressions of the substrate utilization rates; (ii) a change in the enmeshment mechanism by accepting that a fraction of the particulate COD which is *not* adsorbed onto the active organisms, does *not* become enmeshed in the sludge flocs and escapes with the effluent. Accepting only these changes it was found possible to satisfactorily simulate the behaviour of the contact and stabilization reactors of the process under both constant and cyclic conditions of loading.

For design, the general activated sludge model, as applied to the contact stabilization process, requires the process configuration to be completely specified. To aid in the initial design of the process, a preliminary design procedure is presented by means of which the volumes, sludge concentrations and retention times of the contact and stabilization reactors may be determined from five independent parameters which are assumed to govern the process. These are the sludge age, recycle ratio, fractional distribution of the sludge mass between contact and stabilization reactors, daily COD mass load and the average sludge concentration in the process.

NOMENCLATURE

b_h* = endogenous respiration rate (d^{-1})
CMASP = Completely Mixed Activated Sludge Process
CSASP = Contact Stabilization Activated Sludge Process
f = unbiodegradable fraction of the active mass (mg VSS mg VSS^{-1})
f_n = nitrogen fraction of the sludge mass (mg N mg VSS^{-1})
f_{up} = fraction of total influent COD which is in the particulate unbiodegradable form
f_{us} = fraction of the total influent COD which is in the soluble unbiodegradable form
K_{ms}* = maximum specific substrate utilization rate for readily assimilable COD (mg COD mg VSS^{-1} d^{-1})
M = prefix denoting mass, i.e.

$M(S_{ti}) = S_{ti} \cdot Q$ = daily COD mass load (mg COD d^{-1})
$M(X_{vp}) = X_{vp} \cdot V_p$ = mass of sludge in process (mg VSS)

N = general symbol for nitrogen concentration (mg N l^{-1}). Subscripts n or t refer to nitrate or TKN concentrations respectively. Additional subscripts c, e, i or s refer respectively to the values in the contact reactor, effluent, influent or stabilization reactor
O = general symbol for oxygen consumption rate (mg O l^{-1} h^{-1}). Subscripts c, n and t refer to carbonaceous, nitrification and total values respectively. Additional subscripts c, p and s refer respectively to values in the contact reactor, overall process and stabilization reactor
P = COD to VSS ratio (mg COD mg VSS^{-1})
Q = influent flow rate (l d^{-1})
q = waste flow rate (l d^{-1})
R_h = hydraulic retention time (d). Subscripts a or n refer to actual or nominal retention times respectively. Additional subscripts c or s refer to values in the contact or stabilization reactor respectively
R_s = sludge age (d)
r = recycle ratio with respect to average influent flow
S = general symbol for COD concentration (mg COD l^{-1}). Subscript t refers to total concentrations. Additional subscripts c, e, i, s refer respectively to the values in the contact reactor, effluent, influent and stabilization reactor
T = temperature in °C
V = general symbol for volume (l.). Subscripts c, p and s refer to contact reactor, overall process and stabilization reactor respectively
w = waste flow ratio with respect to average influent flow
X = general symbol for volatile sludge concentration (mg VSS l^{-1}). Subscripts a, n and v refer to active volatile, nitrifier and total volatile sludge concentrations respectively. Additional subscripts c, p and s refer respectively to values in the contact reactor, overall process and stabilization reactor

* Additional subscript T or 20 refers to the value at T°C or 20°C.

Y_h = yield coefficient (mg VSS mg COD^{-1})
α = fraction of mass sludge in process in the contact reactor
θ = temperature sensitivity coefficient
μ_{nm}^* = maximum specific growth rate of the nitrifiers (d^{-1})

INTRODUCTION

In the literature, the kinetic theories describing the behaviour of the contact stabilization activated sludge process (CSASP) have been essentially of an *ad hoc* nature. No attempt to describe the behaviour of this process by a general activated sludge kinetic theory has been successful, principally because the theories proposed to date are deficient in themselves. However, the general bi-substrate death–regeneration activated sludge kinetic theory for the process treating principally municipal wastewater, proposed by Dold *et al.* (1980), appears to be sufficiently comprehensive to encompass also the kinetic behaviour of the CSASP treating mainly municipal wastewaters. This paper describes the integration of the CSASP with the general activated sludge theory.

In presenting this paper, it is assumed that the reader has studied the paper setting out the general activated sludge theory (Dold *et al.*, 1980)—only the aspects necessary for the particular requirements of the CSASP will be presented.

INITIAL PROCESS DESIGN

A diagrammatic representation of the CSASP is given in Fig. 1. The contact reactor receives the influent flow and the recycle from the stabilization reactor. In the contact reactor, which has a short nominal hydraulic retention†, a small fraction of the sludge mass removes the bulk of the carbonaceous material from the influent—principally by adsorption and enmeshment. A minor fraction of the adsorbed organic material is metabolized in the contact reactor and consequently the sludge mass contains a high proportion of unmetabolized COD. The effluent from the contact reactor is discharged to the settling tank. The settling tank overflow leaves the process as effluent; the underflow is discharged to the stabilization reactor, which has a long nominal retention time in which the densified mixed liquor is stabilized. Stabilized sludge is returned to the contact reactor via a sludge recycle flow. Close control of the sludge age of the process is possible by hydraulic control, i.e. by wasting an appropriate volume of mixed liquor directly from either the contact or stabilization reactor.

The advantage of the CSASP over the Completely Mixed Activated Sludge Process (CMASP) stems from its configuration. The major fraction of the

† Nominal hydraulic retention time is given by the volume of the reactor divided by the daily average influent flow.

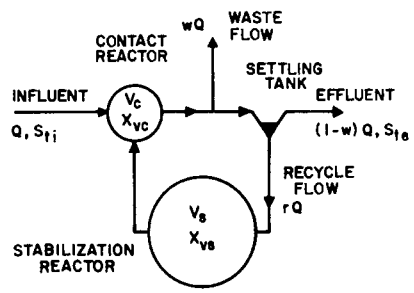

Fig. 1. Diagrammatic representation of the contact stabilization process.

sludge mass in the CSASP system is contained in the stabilization reactor in a densified form, giving a correspondingly smaller volume to the whole system. Furthermore, if the excess sludge is wasted from the contact reactor, as shown in Fig. 1, the overall process oxygen demand is slightly reduced because the sludge mass in the contact reactor contains a relatively high fraction of unmetabolized COD.

The CSASP is a spatially dependent system even under steady flow and load conditions. The concentration of sludge and the food/micro-organism ratio differ significantly in the contact and stabilization reactors; these parameters are dependent on the sludge recycle rate and the fractional distribution of the mass of sludge between the two reactors. Therefore, unlike the CMASP which essentially is defined by the sludge age and the organic load in the process, in the CSASP the process definition must include, in addition to the above parameters, the recycle ratio, r, and some parameter fixing the fractional distribution of the mass of sludge between the contact and stabilization reactors. Ohron & Jenkins (1972) selected the fraction of the mass of sludge in contact reactor relative to the total mass of sludge in the process, α, to define the fractional parameter, i.e.

$$\alpha = V_c X_{vc}/(V_c X_{vc} + V_s X_{vs}) \quad (1)$$

where

V_c, V_s = volumes of the contact and stabilization reactors respectively (l.)
X_{vc}, X_{vs} = volatile sludge concentrations in the contact and stabilization reactors respectively (mg VSS l^{-1}).

It will be apparent from the above, that the design of a specific CSASP is not as straightforward as the CMASP and must proceed on a trial and error basis. In designing a CSASP configuration it is particularly useful to have a procedure for initially estimating the sizes of the reactors and their respective sludge concentrations in order to decide whether the liquid solid separation efficiency in the settling tank and the actual hydraulic retention time in the contact reactor are within acceptable limits.

A basis for making an initial estimate of the reactor sizes is to accept that the *CSASP produces the same mass of sludge as the CMASP for the same sludge age,*

R_s, and daily organic mass load, $M(S_{ti})$. This assumption is based on the findings of Gujer & Jenkins (1975a) and has been verified during this investigation. Therefore, an estimate of the total mass of sludge in the process $M(X_{vp})$ can be obtained from the steady state equations for the CMASP (Marais & Ekama, 1976), i.e.

$$M(X_{vp}) = M(S_{ti})R_s\left\{\frac{Y_h(1 + f b_{hT} R_s)}{(1 + b_{hT} R_s)} \times (1 - f_{us} - f_{up}P) + f_{up}\right\} \quad (2)$$

where

$M(X_v)$ = mass of volatile sludge in process (mg VSS)
$= X_{vp}V_p$
X_{vp} = average process volatile sludge concentration (mg VSS l^{-1})
V_p = volume of process (l.)
$M(S_{ti})$ = daily organic mass load (mg COD d^{-1})
$= Q \cdot S_{ti}$
S_{ti} = total influent COD concentration (mg COD l^{-1})
R_s = sludge age (d)
Y_h = yield coefficient (mg VSS mg COD^{-1})
$= 0.45$
f = unbiodegradable fraction of the active volatile mass (mg VSS mg VSS^{-1})
$= 0.20$
b_{hT} = endogenous respiration rate at T°C (d)
$= b_{h20}\theta^{(T-20)}$
b_{h20} = endogenous respiration rate at 20°C
$= 0.24$
θ = temperature sensitivity coefficient
$= 1.029$
T = temperature (°C)
f_{us} = soluble unbiodegradable fraction of the influent COD (mg COD mg COD^{-1})
f_{up} = particulate unbiodegradable fraction of the influent COD (mg VSS mg COD^{-1})
P = COD to VSS ratio (mg COD mg VSS^{-1})

Once an estimate of $M(X_{vp})$ is available, a decision must be made on the overall *mean sludge concentration, X_{vp},* for the process. The overall volume of the CSASP, V_p, is determined by

$$V_p = M(X_{vp})/X_{vp} \quad (3)$$

where

$$V_p = V_s + V_c \quad (4)$$

and

$$V_pX_{vp} = V_cX_{vc} + V_sX_{vs}. \quad (5)$$

If X_{vp} for the CSASP is chosen to be the same as that for a CMASP the volumes of the two processes will be identical, resulting in no space saving. Consequently, X_{vp} for the CSASP usually is selected to be appreciably higher than that normally accepted for the CMASP in order to gain a plant volumetric advantage. Higher X_{vp} concentrations for the CSASP are permissible because the settling tank of the process has to deal with the relatively low concentration of sludge from the contact reactor.

Where the sludge age, R_s, of the CSASP is controlled by wasting sludge directly from the contact reactor, i.e. hydraulic control of the sludge age, the sludge age of the process is given by

$$R_s = \frac{\text{mass of sludge in process}}{\text{mass of sludge wasted per day}} = X_{vp}V_p/(X_{vc}q) \quad (6)$$

where

q = waste flow rate ($l\,d^{-1}$)

In the analysis of the CSASP significant simplification in the formulations is attained by expressing q as a fraction of the average influent flow rate, i.e.

$$q = wQ \quad (7)$$

where

Q = average influent flow ($l\,d^{-1}$)
w = sludge waste flow rate from the contact reactor as a fraction of the average influent flow rate.

Hence, for a given sludge age, w is given by

$$w = X_{vp}V_p/(R_sQX_{vc}) \quad (8)$$

In order to size the two reactors of the CSASP, a decision on the two additional independent parameters α and r is required. Knowing α, r, R_s and X_{vp} as well as V_p, which can be determined from equations (2) and (3), then by doing a sludge mass balance around each reactor and manipulating equations (4)–(7), the concentration of the sludge in, and the volumes of the two reactors can be expressed in terms of the five known parameters, i.e.

$$V_c = V_p\alpha(1 + r - w)/(\alpha + r - \alpha w) \quad (9)$$

$$V_s = V_p r(1 - \alpha)/(\alpha + r - \alpha w) \quad (10)$$

$$X_{vc} = X_{vp}(\alpha + r - \alpha w)/(1 + r - w) \quad (11)$$

$$X_{vs} = X_{vp}(\alpha + r - \alpha w)/r \quad (12)$$

$$X_{vs} = X_{vc}(1 + r - w)/r. \quad (13)$$

An expression for w in equations (9)–(13) can be derived as follows:

Substituting equation (5) for V_pX_{vp} in equation (8):

$$w = (X_{vc}V_c + X_{vs}V_s)/(R_sQX_{vc}). \quad (14)$$

Substituting equation (13) for X_{vs} and equation (10) for V_s into equation (14) and rearranging, yields:

$$w = V_p(1 + r - w)/\{R_sQ(\alpha + r - \alpha w)\}. \quad (15)$$

Under normal operating conditions, αw is small relative to $(\alpha + r)$. Consequently, ignoring αw in equation (15) and solving for w, an expression for w in terms of

the known parameters is obtained, i.e.

$$w = (1 + r)/\{1 + (\alpha + r)QR_s/V_p\}. \quad (16)$$

From equations (9) and (10), the actual and nominal retention times in the two reactors can be found, i.e.

$$R_{hac} = V_p(1 + r - w)/[(1 + r)(\alpha + r - \alpha w)Q] \quad (17)$$

$$R_{has} = V_p(1 - \alpha)/[(\alpha + r - \alpha w)Q] \quad (18)$$

$$R_{hnc} = (1 + s) \cdot R_{hac} \quad (19)$$

$$R_{hns} = R_{has} \quad (20)$$

where

R_h = hydraulic retention time (d). Second subscripts a or n refer to actual or nominal values respectively. Additional subscripts c or s refer to contact or stabilization reactors respectively.

From the equations set out above estimates of V_c, V_s, X_{vc}, and X_{vs} in terms of the values α, r, $M(S_{ti})$, X_{vp} and R_s are now available and constitute an initial design. Checks can be made to ensure that the actual hydraulic retention in the contact reactor is adequate and that the densification ratio in the settling tank is not too great.

Experience with experimental plants and the general activated sludge model as applied to the CSASP, has indicated that this preliminary design procedure predicts X_{vc} and X_{vs} accurately. Also, the average process carbonaceous oxygen demand for the system approximately equals that for the equivalent CMASP [i.e. for the same R_s and $M(S_{ti})$]. However, the procedure provides no estimation of the relative oxygen demands in the two reactors, nor the COD, TKN and nitrate concentration in the reactors or effluent under constant or cyclic loading conditions. Under constant flow conditions these process variables may be estimated from models with constants determined on an *ad hoc* basis (Gujer & Jenkins, 1975a, b). However, under cyclic loading conditions the only reliable procedure for determining these process variables is by utilizing the general activated sludge model as applied to the CSASP.

EXPERIMENTAL INVESTIGATION

It has been shown that there are five major parameters which influence the response of the CSASP, i.e. daily COD load, $M(S_{ti})$, sludge age, R_s, temperature T, sludge recycle rate, r, and the fractional distribution of sludge mass between the contact and stabilization reactors in terms of, α. For this investigation it was decided that the temperature, r and α would be kept constant, while the sludge age and daily COD load pattern would be varied. The reason for maintaining r and α constant was that Gujer & Jenkins (1975a) reported that these two parameters have less effect on the efficiency of carbonaceous material removal by the process than the other three. Theoretically, this observation is also consistent with the bi-substrate theory (Dold *et al.*, 1980). Although r and α have a marked effect on the contact reactor hydraulic retention time, the particulate carbonaceous substrate, which forms the bulk of the influent COD, is either adsorbed by the organisms or enmeshed in the sludge flocs and removed from the effluent in the settling tank.

Adsorption and enmeshment are rapid processes, so that they are expected to be near completion even in relatively short actual hydraulic retention times. The removal of the soluble COD fraction in the influent by the contact reactor *is* affected by the length of the contact time: any soluble COD concentration not metabolized during the contact period in the contact reactor escapes with the effluent flow. However, as only about 25% of the biodegradable COD is in soluble form (Dold *et al.*, 1980) and the removal is rapid, the escape of the soluble COD concentration is unlikely to affect the overall COD removal efficiency.

With regard to α, a value of 0.1 was selected as with this value only one tenth of the mass of sludge in the process is responsible for the initial removal of the carbonaceous material from the influent. It represents, therefore, an extreme situation and constitutes a severe test of the predictive capacity of the model.

With regard to the choice of r, a high value ($r > 4$) in the CSASP results in a smaller relative difference between the concentrations of sludge in the contact and stabilization reactors and the process approximates the CMASP which would tend to detract from the uniqueness of the CSASP configuration. In contrast, a low recycle ratio ($r < 1$) results in a low process nitrification efficiency, as only a small fraction of the influent ammonia is recycled to the stabilization reactor in which the bulk of the sludge mass is retained (Gujer & Jenkins, 1975b). Consequently, a recycle ratio of 2:1 with respect to average flow was selected.

The experimental investigation was to be undertaken at 20°C. To ensure complete nitrification of the recycled ammonia in the stabilization reactor, sludge ages longer than about 4 days are required. Consequently, sludge ages of 6 and 10 days were selected.

If the CSASP operates under cyclic flow conditions, the actual hydraulic retention time in the contact reactor is reduced during the peak flow period. Should the actual hydraulic retention time under peak flow conditions become too short, particulate COD removal by adsorption and enmeshment and soluble COD removal by metabolism will be insufficient, resulting in a poor effluent quality. Consequently a lower limit to the minimum actual hydraulic retention time in the contact reactor needs to be set. To satisfy this lower limit, it will be found that lower values of X_{vp} or higher values of α need to be chosen as the peak/average flow ratio increases, than would be required under the average flow conditions.

In this experimental investigation, the minimum actual hydraulic retention time in the contact reactor was set at about 20 min under an expected peak/average flow ratio of 1:1.5. With this restriction, the chosen design parameters α, r, R_s and $M(S_{ti})$, the design of the experimental CSASP units was obtained by a trial and error procedure. All the conditions could be met only when X_{vp} was less than about 2000 mg VSS l^{-1}—a relatively low value. By doubling α to 0.2, and keeping the minimum actual hydraulic retention time in the contact reactor at 20 min under the peak/average flow ratio of 1:1.5, X_{vp} can be increased to 3800 mg VSS l^{-1}, giving a more practical design. However, from a model verification point of view, the latter design would not have provided as severe a test on the predictive capacity of the model as the former.

The chosen design parameters of the experimental units are given in Table 1 and a diagrammatic layout of the units is shown in Fig. 2.

The experimental investigation was divided into two phases: (a) a phase during which the two experimental units were operated under constant flow and load conditions, and (b) a phase during which one of the units was operated under cyclic flow and load conditions.

Table 1. Process design parameters for the Laboratory CSASP units

Parameter Name	Symbol	Units	Sludge age 6 days	Sludge age 10 days
1. Sewage type			Unsettled	Unsettled
2. Influent COD	S_{ti}	mg COD l^{-1}	500	500
3. Influent TKN	N_{ti}	mg N l^{-1}	~50	~50
4. Average influent flow	Q	$l\,d^{-1}$	36	24
5. Temperature	T	°C	20	20
6. Sludge age	R_s	d	6	10
7. Waste flow ratio	w	—	0.092	0.083
8. Fractional distribition of sludge in process	α	—	0.10	0.10
9. Recycle ratio	r	—	2.0	2.0
10. Volumes		l.		
Process	V_p	l.	14.3	14.3
Contact reactor	V_c	l.	2.0	2.0
Stabilization reactor	V_s	l.	12.3	12.3
11. Average hydraulic retention times	R_h	h		
Contact:				
Actual	R_{hac}	h	0.44	0.67
Nominal	R_{hnc}	h	1.32	1.98
Stabilization:				
Actual	R_{has}	h	4.07	6.27
Nominal	R_{hns}	h	4.07	6.27
12. Length of test period	—	d	23	25

(a) Constant flow and load conditions were established by feeding the required volume of sewage feed per day at a constant rate over the day. The average values of the daily measurements of the process variables in the contact and stabilization reactors and in the effluent of the 6 and 10 day sludge units are given in Table 2, the length of the test period having been about 25 days.

(b) In the cyclic loading tests the 6 day sludge age unit was operated under two different influent cyclic flow patterns: (i) a square wave pattern, and (ii) a sine wave pattern. In both cases the daily influent COD mass was the same and equal to that fed during the constant flow test, i.e. 18,000 mg COD d^{-1}.

(i) The *square wave loading pattern* was obtained by dividing the daily influent feed volume of 36 l. between two pumps—one operating at a rate of 18 $l\,d^{-1}$ over the full 24 h period and the other at 36 $l\,d^{-1}$ for a period of 12 h only.

Measurements of the process variables in the contact and stabilization reactors and in the effluent were made at regular intervals over a 24 h period—a typical set of data is shown in Fig. 3.

(ii) The *sine wave loading pattern* was achieved by means of a specially designed pump that produced an approximate sine wave flow with an amplitude of about 0.5 times the average flow. A typical set of data observed over a 24 h cycle under sine wave influent flow conditions is shown in Fig. 4.

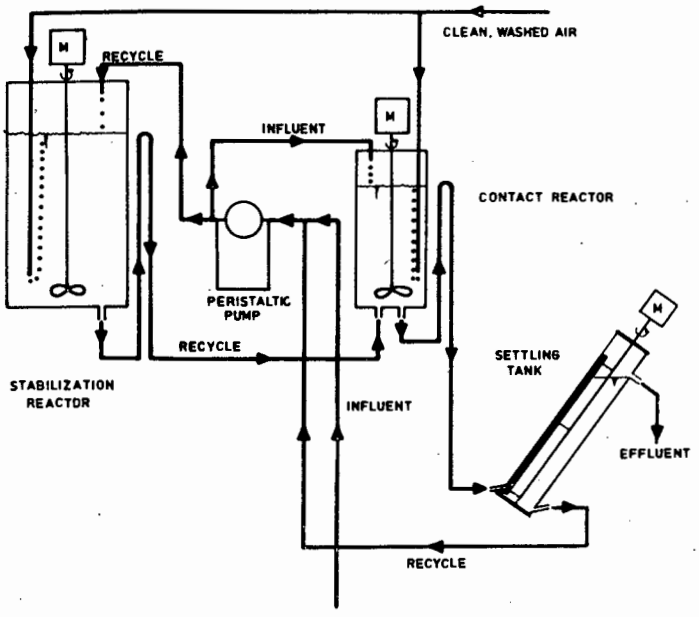

Fig. 2. Diagrammatic representation of the laboratory scale contact stabilization process.

Table 2. Averages of process variable measurements observed in laboratory scale contact stabilization units. The corresponding predictions of the general model are also given

Process variable			Constant flow and load conditions, Sludge age 6 Days		10 Days	
	Position	Symbol	Measured	Predicted	Measured	Predicted
COD mg COD l^{-1}						
	Influent	S_{ti}*	512	512	496	496
	Contact	S_{tc}	62	60	52	57
	Effluent	S_{te}*	90	81	61	75
	Stabilization	S_{ts}	54	45	42	43
TKN mg N l^{-1}						
	Influent	N_{ti}*	56	56	47	47
	Contact	N_{tc}	11	15	10.5	12
	Effluent	N_{te}*	15	15	12	12
	Stabilization	N_{ts}	1.7	3	4.8	3
Nitrate mg N l^{-1}						
	Influent	N_{ni}	0.0	0.0	0.0	0.0
	Contact	N_{nc}	27	27	22	23
	Effluent	N_{ne}	27	27	23	23
	Stabilization	N_{ns}	36	37	29	31
MLVSS mg VSS l^{-1}						
	Contact	X_{vc}	1301	1489	1478	1389
	Stabilization	X_{vs}	1772	2099	2073	1989
	Process	X_{vp}	1706	2016	1990	1903
Oxygen Demand (mg O l^{-1} h^{-1})						
Carbon	Contact	O_{cc}	31	29	24	23
Carbon	Stabilization	O_{cs}	22	23	16	16
Carbon	Process	O_{cp}	23	24	17	17
Nitrif.	Contact	O_{nc}	30	24	18	19
Nitrif.	Stabilization	O_{ns}	10	11	5	5
Nitrif.	Process	O_{np}	13	13	7	8
Total	Contact	O_{tc}	61	54	42	42
Total	Stabilization	O_{ts}	32	34	21	22
Total	Process	O_{tp}	36	37	24	25
	Mass balances	COD†	96%	100%	97%	100%
		N‡	94%	100%	96%	100%

* Refers to unfiltered samples.
† Based on a COD/VSS ratio of 1.48.
‡ Based on TKN/VSS ratio (f_n) of 0.10.

MODEL VERIFICATION

The general kinetics of the activated sludge process including nitrification described by Dold *et al.* (1980) were incorporated into a general model for the CSASP (in the form of a computer program). When this model, as well as its associated kinetic constants, was applied to simulate the behaviour observed in the experimental CSASP units described above, the following observations were made:

Changes in kinetic constants

The predictions of the response of the contact reactor is very sensitive to the values of the maximum specific growth rate of the nitrifiers (μ_{nm20}) and the maximum utilization rate of soluble carbonaceous substrate (K_{ms20}).

With regard to μ_{nm20}, Dold *et al.* found an *average* value of 0.65 d^{-1} for data. The value of μ_{nm20} associated with each batch of sewage can be determined by obtaining the best fit between experimental and predicted TKN and nitrate concentrations. From a comparison of many experimental and predicted responses, it became evident that the value of μ_{nm20} often changes for each batch of sewage probably due to changes in the content of inhibitory substances. In this investigation, it was found that the best overall correspondence between experimental and predicted TKN and nitrate concentrations was obtained when $\mu_{nm20} = 0.55\ d^{-1}$. All the CSASP simulations are based on this value.

With regard to K_{ms20}, Dold *et al.* found that a value of 8.0 mg COD mg VSS d^{-1} gave the best correspondence between experimental and predicted oxygen consumption rates for single and series CMAS processes. When this value for K_{ms20} was utilized to simulate the behaviour of the CSASP under cyclic loading conditions it was found that the predicted oxygen consumption rate in the contact reactor (O_{tc}) showed a marked cyclic variation over the day—a result in conflict with the experimental observations. Also, the variation in the predicted soluble COD con-

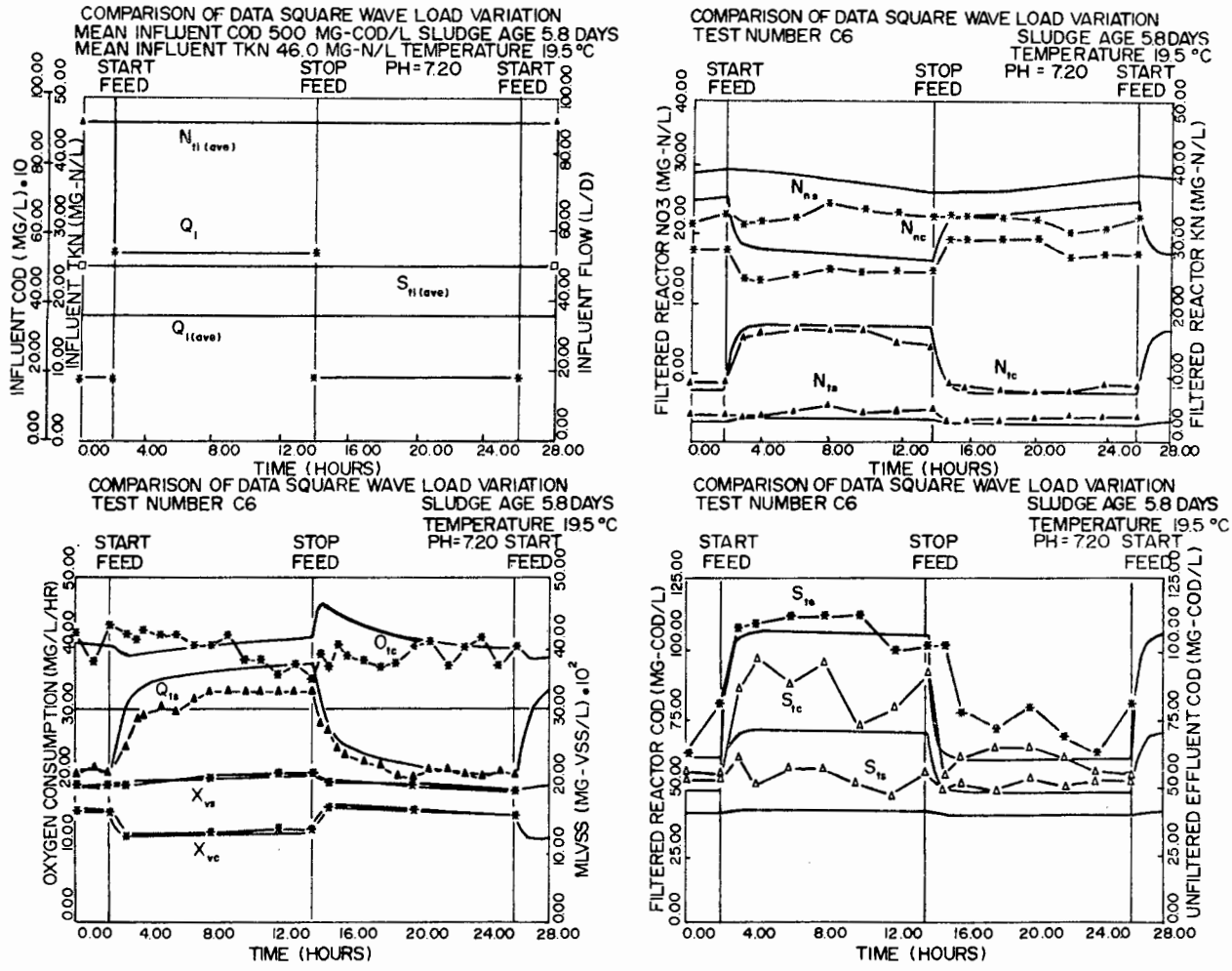

Fig. 3. Comparison of experimental and predicted responses of the contact stabilization process under daily cyclic square wave loading conditions at 20°C.

centration in the contact reactor (S_{tc}) showed a far greater degree of attenuation than the experimental data. The best correspondence between predicted and experimental O_{tc} and S_{tc} responses was obtained when $K_{ms20} = 2.0$ mg COD mg VSS d^{-1}. When this value was incorporated in the CMASP model, predictions of the precipitous decrease in the oxygen consumption rate at feed termination in square wave cyclically loaded single reactor CMAS units (see Dold *et al.*, 1980) was not accurately predicted. No explanation can be advanced for this apparent discrepancy between the K_{ms20} values for the CSAS and CMAS processes.

The kinetic constants μ_{nm20} and K_{ms20} were the only two which required adjustment of their values. The need for adjusting μ_{nm20} is not necessarily indicative of a deficiency in the formulations of the general model, because there appears to be strong evidence that μ_{nm20} does in fact change not only between different sources but also between batches of sewage obtained from the same source—the sensitivity of the nitrifiers to inhibitory or toxic substances in the wastewater is well documented in the literature. However, the need for changing K_{ms20} for the CSASP is indicative of a deficiency in the formulations of the general model. The lowering of K_{ms20} indicates that the soluble carbonaceous substrate is utilized at a slower rate in the contact reactor of a CSASP than in the first reactor of a multiple CMASP. However, once the different value of K_{ms20} is accepted, the general model is capable of describing the CSASP under both constant and cyclic conditions of loading.

Modification to enmeshment mechanism

A conceptual modification had to be made to the general activated sludge model in order to satisfactorily simulate general CSASP behaviour. In the experimental data observed in the CMASP, it was found that there was very little difference between the filtered and unfiltered effluent COD concentration. Consequently, in the general model, it was assumed that all the unadsorbed particulate COD remains enmeshed in the sludge flocs, is densified with the sludge in the settling tank and recycled to the reactor. However, the CSASP experimental data (see Table 2 and Figs 3 and 4) show a marked difference between

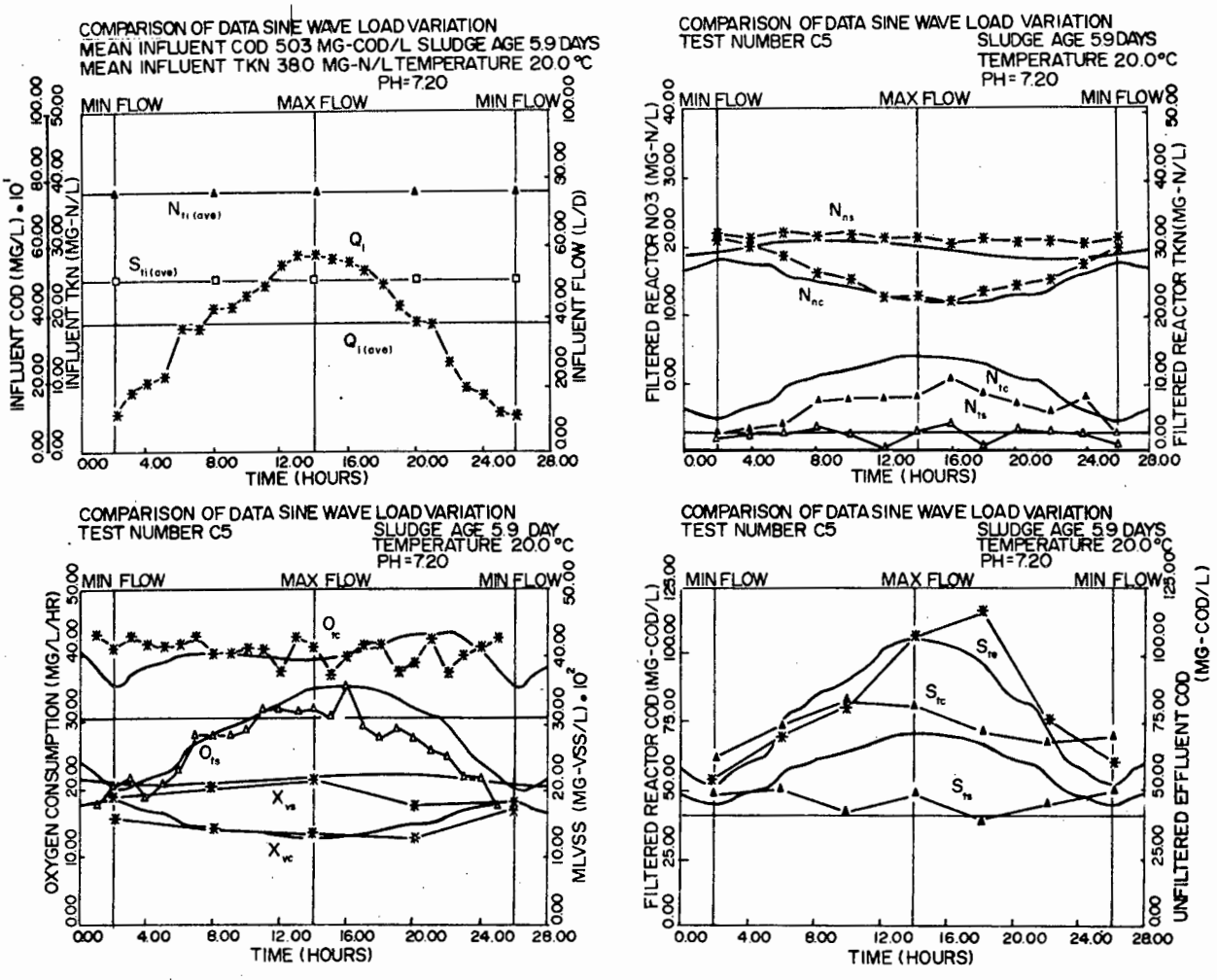

Fig. 4. Comparison of experimental and predicted responses of the contact stabilization process under daily cyclic sine wave loading conditions at 20°C.

filtered and unfiltered effluent COD concentrations, the unfiltered values being always significantly higher than the filtered values*. This appeared to indicate that the flocculation and enmeshment of the particulate substrate was not complete in the contact reactor. This effect was empirically incorporated into the model by hypothesizing that a fraction of the particulate COD *not* adsorbed onto the active mass does *not* become enmeshed in the sludge flocs and escapes with the effluent. A good correspondence between predicted and measured filtered and unfiltered effluent COD concentrations was obtained when this fraction was assumed to be 0.50. The effect appears to have relevance to only the CSASP because in series or single reactor CMASP, the retention times are sufficiently long and sludge concentrations sufficiently high for adsorption and enmeshment to be virtually complete before solid–liquid separation takes place.

* The comparison is based on the assumption that the filtered contact and filtered effluent COD concentrations are equal.

General CSASP model

The changes discussed above were accepted and incorporated in the CSASP model. The theoretical predictions of this model with the corresponding experimental data observed under constant and cyclic loading conditions at 20°C are given in Table 2 and Figs 3 and 4 respectively. The comparison of the predicted and experimental data is discussed below.

COMPARISON OF EXPERIMENTAL AND THEORETICAL DATA

Constant flow conditions (Table 2)

In general there is a good correspondence between predicted and experimental results at both 6 and 10 days sludge age. The predicted sludge concentration in the 6 day sludge age unit is higher than the corresponding experimental data. However, subsequently, when the unit was operated under cyclic loading conditions with the sludge age remaining at 6 days, the experimental sludge concentrations stabilized at values very close to those predicted by the model (see Figs 3 and 4). Hence the low experimental values

measured during this period are likely to be a consequence of the variation in behaviour usually associated with biological systems.

The over-prediction of the TKN concentration in the contact reactor, N_{tc}, appears to indicate that more nitrification took place in the experimental unit than the model predicts. However, this is not reflected in the measured and predicted nitrate concentrations. The reason for this discrepancy is that the nitrogen fraction of the waste sludge, f_n, in the experimental unit was slightly higher, i.e. 0.12 mg N mg VSS^{-1}, than the value incorporated in the general model, i.e. 0.10 mg N mg VSS^{-1}. This results in a greater mass of nitrogen being removed from the experimental unit via the waste sludge than predicted by the model. This difference is reflected in the effluent TKN concentrations. Furthermore, by assuming an f_n value of 0.12 mg N mg VSS^{-1} for the experimental unit, an improved nitrogen balance will be obtained (Table 2).

The experimental nitrification oxygen demand may be calculated from the experimental data by considering a nitrate mass balance over the contact or stabilization reactors. The carbonaceous value is given by the difference between the total and nitrification values. A comparison between the experimental and predicted values is given in Table 2. The contact nitrification oxygen demand (O_{nc}) calculated from the nitrate measurements (N_{nc}), is extremely sensitive to changes in the values of these measurements—a 1 mg N l^{-1} difference in N_{nc} results in a 10.7 mg O l^{-1} h^{-1} difference in O_{nc}. In contrast, the nitrification oxygen demand in the stabilization reactor (O_{ns}) is relatively insensitive to changes in the input and output nitrate concentrations. Taking into account these factors, it is clear that there is a good correspondence between the model predictions and experimental observations.

Cyclic flow and load conditions (Figs 3 and 4)

In general the correspondence between the predicted and experimental responses under both square and sine wave loading conditions is very good. A detailed discussion of the comparison of each process variable is given below.

1. *COD concentration.* As in the constant flow and load tests, a difference between the filtered COD concentration in the contact reactor and the unfiltered value in the effluent is apparent. It appears that the empirical partial enmeshment modification in the CSASP model allows accurate predictions of the effluent COD concentration (both filtered and unfiltered) even under different cyclic loading conditions.

2. *MLVSS concentration.* The correspondence between the predicted and experimental MLVSS concentrations is excellent in both cyclic tests. An interesting observation is the significant "washing out" effect of the MLVSS from the contact reactor during the peak flow period. It was stated above that as the recycle ratio increased in the CSASP, the process approached the CMASP. As the recycle flow was kept at twice the average influent flow throughout the daily cycle, the recycle *ratio* varied over the cycle resulting in fluctuating MLVSS concentrations in the contact stabilization reactors. For example, under the square wave loading conditions (Fig. 3), the recycle ratio was 4:1 (2 × 36/18) during the low flow period and 1.33:1 (2 × 36/54) during the peak flow period. The period of high recycle ratio (4:1) caused the CSASP to approach the CMASP in behaviour so that the difference between the sludge concentrations in the contact and stabilization reactors was small. In contrast, the low recycle ratio period causes a pronounced deviation from the CMASP so that the difference between the sludge concentration in the contact and stabilization reactors is large.

3. *Oxygen consumption rate.* In the contact reactor, the experimental total oxygen consumption rate, O_{tc} remains virtually constant throughout the cycle. Compared to the CMASP, such a high degree of attenuation in the oxygen demand is unexpected under cyclic influent loading conditions. However, considering square wave loading conditions (Fig. 3) this behaviour can be explained as follows: Upon commencement of the peak flow period, the availability of carbonaceous and ammoniacal substrates increases in the contact reactor, resulting in a greater activity of the heterotrophic and nitrifying organisms. However, concomitant with the higher sludge activity, the sludge concentration (X_{vc}, X_{nc}) is reduced. The net result is a relatively constant total oxygen consumption rate.

Dividing the experimental total oxygen consumption rate measured in the contact reactor (O_{tc}) into the carbonaceous (O_{cc}) and nitrification (O_{nc}) components by deducting O_{nc} from O_{tc} led to widely fluctuating results—O_{nc} is extremely sensitive to small variations in the measured nitrate concentration. Consequently, only the predicted and experimental O_{tc} responses could be reliably compared.

The model satisfactorily predicts the observed attenuated O_{tc} response. However, under square wave loading conditions (Fig. 3), the model incorrectly predicts an increase in O_{tc} immediately after cessation of the peak flow period. In the theoretical model this increase is caused by the increase in sludge concentration (X_{vc}, X_{nc}) at a time when the carbonaceous and ammoniacal substrates concentrations are still high from the peak flow period. Considering the difficulties associated with accurately measuring oxygen consumption rates in the contact reactor (Ekama & Marais, 1979), the discrepancy between the predicted and experimental O_{tc} responses is as likely to be a consequence of a deficiency in the theoretical model as experimental error.

In both cyclic tests, the total oxygen consumption rate in the stabilization reactor (O_{ts}) is slightly overpredicted. Dividing the experimental O_{ts} response into the carbonaceous (O_{cs}) and nitrification (O_{ns}) components is possible because O_{ns} is relatively insensitive to small variations in the nitrate concentration (N_{ns}). Considering the square wave test, a

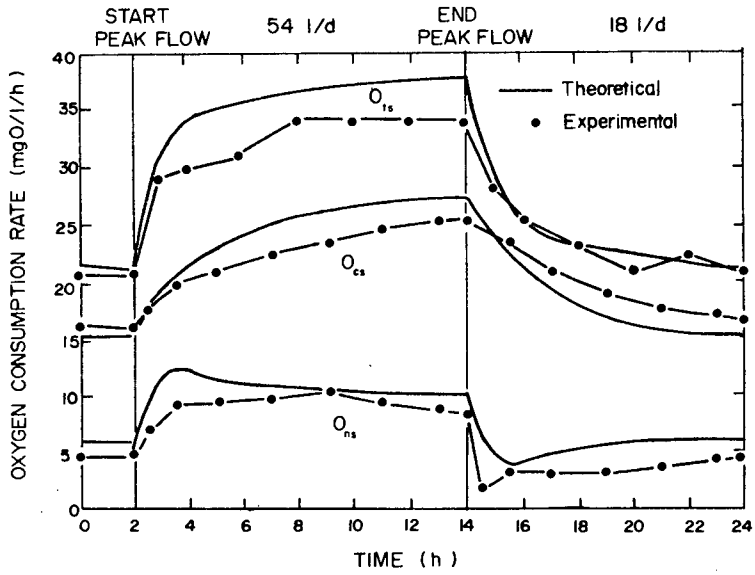

Fig. 5. Comparison of the experimental and predicted carbonaceous nitrification and total oxygen consumption rates in the stabilization reactor of the CSASP under square wave loading conditions at 20°C.

comparison of the predicted and experimental O_{ts}, O_{ns} and O_{cs} responses is given in Fig. 5 and shows a satisfactory correlation.

4. *TKN and nitrate concentrations.* In general, the theoretical model satisfactorily predicts the experimental TKN and nitrate concentrations in the contact and stabilization reactors under both cyclic square and sine wave loading conditions. In the former test (Fig. 3), the over-prediction of the nitrate concentration in the contact (N_{nc}) and stabilization reactor (N_{ns}) is most likely attributable to a slightly higher nitrogen fraction in the sludge (f_n) of the experimental unit than assumed theoretically. In the latter test (Fig. 4), an improved prediction of the TKN and nitrate concentrations in contact reactor (N_{tc}, N_{nc}) would be obtained with a slightly higher μ_{nm20} than assumed (0.55 d^{-1}) for this particular batch of sewage.

CONCLUSIONS

This paper provides a means whereby initial estimates can be made of the volumes of and the sludge concentrations in the contact and stabilization reactors of a CSASP from the six independent design parameters assumed to govern the behaviour of the process, i.e. sludge age, R_s, recycle ratio, r, fractional distribution of the sludge mass between the two reactors defined by α, daily COD mass load, $M(S_{ti})$ and the average process sludge concentration, X_{vp}. The sixth design parameter, i.e. temperature, was not considered in this paper.

Two changes to the general activated sludge kinetic model proposed by Dold *et al.* (1980) were accepted, i.e. (1) a change in the value of one of the kinetic constants in the expressions of the carbonaceous substrate utilization rates; and (2) a change in the enmeshment mechanism by accepting that a fraction of the particulate COD which does *not* become adsorbed onto the active mass, does *not* become enmeshed in the sludge flocs and escapes with the effluent.

With these changes it was found that the model is sufficiently general to give a good description of the behaviour of the CSASP under constant and cyclic conditions of loading.

The investigation into the cyclic behaviour of the CSASP indicated that the peak flow periods reduce the carbonaceous material removal and nitrification efficiencies of the process in two ways, i.e. by reducing (i) the actual hydraulic retention as well as (ii) the sludge concentration in the contact reactor. This behaviour of the process results in the effluent COD and TKN concentrations being very sensitive to cyclic loading conditions. More stable effluent qualities under cyclic loading conditions may be produced by increasing the design parameters α and r and reducing X_{vp}. However, such changes reduce the specific advantages that the CSASP has over the CMASP, and produce configurations conforming more to the behavioural characteristics of the CMASP.

A major difficulty in applying existing carbonaceous material removal and nitrification models for the CSASP, for example those proposed by Gujer & Jenkins (1975a, b), to design, is an accurate estimate of the values of the constants associated with these models under the environmental conditions in the field. These difficulties are also encountered in the application of the computer model to design—although the *kinetic constants* of the carbonaceous material removal mechanisms remain relatively unchanged for different domestic sewages, the process

response does depend on the influent sewage characteristics, such as the unbiodegradable soluble and particulate COD fractions (f_{us} and f_{up} respectively). Also, the maximum specific growth rate of the nitrifiers at 20°C (μ_{nm20}) has been found to vary considerably between different sewages. It appears that the only way of overcoming these difficulties is to determine these constants in laboratory scale investigations utilizing the wastewater to be treated.

A further difficulty in applying the existing models of the CSASP to full scale design is an estimation of the influence of cyclic loading conditions on the process behaviour. Once the sewage characteristics have been established, the general activated sludge theory as applied to the CSASP allows the prediction of the dynamic behaviour of the process under cyclic loading conditions. This model is very cumbersome and can only be utilized in the form of a computer program.

Design engineers prefer simple design charts and models. Existing models and the initial design procedure presented in this paper satisfy this preference. However, dynamic solutions of the process behaviour cannot be obtained by simplistic models, computer models have to be employed, if such solutions are required. The use of a simplistic model for the preliminary determination of the independent process variables and subsequent analysis of the dynamic behaviour of the process by computer models seems a satisfactory compromise and indeed appears to be a logical approach to design.

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REFERENCES

Dold P. L., Ekama G. A. & Marais G. V. R. (1980) The activated sludge process Part 1. A general model for the activated sludge process. Proc. 10th Int. Conf. I.A.W.P.R., Toronto. In *Prog. Wat. Technol.* Vol. 12, 1980.

Ekama G. A. & Marais G. V. R. (1979) Letter to the Editor. *Water S.A.* **5**, 57–60.

Gujer W. & Jenkins D. (1975a) The contact stabilization activated sludge process—oxygen utilization, sludge production and efficiency. *Water Res.* **9**, 553–560.

Gujer W. and Jenkins D. (1975b) A nitrification model for the contact stabilization activated sludge process. *Water Res.* **9**, 561–566.

Marais G. V. R. & Ekama G. A. (1976) The activated sludge process. Part 1—Steady state behaviour. *Water S.A.* **2**, 163–200.

Ohron D. M. & Jenkins D. (1972) The mechanism and design of the contact stabilization activated sludge process. *Adv. Wat. Pollut. Res.* **6**, 353–362.

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THE ACTIVATED SLUDGE PROCESS—3

SINGLE SLUDGE DENITRIFICATION

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Abstract—The general aerobic bi-substrate active-site death-regeneration activated sludge model including nitrification of Dold *et al.* (*Prog. Wat. Technol.* **12**, 47–77, 1980) is extended to include the kinetic behaviour of the denitrification process in single sludge systems. The extension requires a change in the value of only one of the kinetic constants (K'_{mp}) in the expression for the particulate substrate utilization rate when the environment becomes anoxic. The extended model simulates very closely the response of the multi-reactor nitrification–denitrification process configurations under both constant and cyclic flow and load conditions. Under constant flow and load conditions, the denitrification response predicted can be reduced to that approximated by a zero order reaction $dN/dt = -KX_a$ with two rates in the primary and one in the secondary anoxic reactor respectively.

NOMENCLATURE

a = recycle ratio
b_h = endogenous respiration rate constant for heterotrophs (mg X_a·mg X_a^{-1}·d^{-1})
b'_h = death rate constant for heterotrophs (mg X_a·mg X_a^{-1}·d^{-1})
b_n = death rate constant for nitrifiers (mg X_n·mg X_n^{-1}·d^{-1})
f = inert residue fraction in endogenous respiration approach (mg VSS·mg VSS^{-1}) = 0.2
f' = inert residue fraction in death regeneration approach (mg VSS·mg VSS^{-1})
f_{cs} = ratio easily biodegradable (S_{bsi}): total biodegradable (S_{bi}) COD concentration in influent (mg COD·mg COD^{-1})
f_n = nitrogen/VSS ratio in sludge = 0.1 mg NH$_3$–N·mg VSS^{-1}
f_{us} = unbiodegradable soluble COD fraction in influent (mg COD·mg COD^{-1})
f_{up} = unbiodegradable particulate COD fraction in influent (mg VSS·mg COD^{-1})
t = time (d or h)
t_p = duration of primary phase in a pre-denitrification reactor (h)
A = specific rate of utilization of easily biodegradable material (mg COD·mg X_a^{-1}·d^{-1})
B = specific rate of adsorption of slowly biodegradable material (mg COD·mg X_a^{-1}·d^{-1})
C = specific rate of utilization of stored biodegradable material (mg COD·mg X_a^{-1}·d^{-1})
D = specific rate of release of COD due to lysis (mg COD·mg X_a^{-1}·d^{-1})
E = specific rate of utilization of ammonia for nitrification (mg NH$_3$–N·mg X_n^{-1}·d^{-1})
F = specific death rate of nitrifiers (mg X_n·mg X_n^{-1}·d^{-1})
K = denitrification rate constant (mg NO$_3$–N·mg VSS^{-1}·h^{-1})
K_1 = denitrification rate constant in primary phase (mg NO$_3$–N·mg X_a^{-1}·h^{-1})
K_2 = denitrification rate constant in secondary phase (mg NO$_3$–N·mg X_a^{-1}·h^{-1})
K_3 = denitrification rate constant in post denitrification reactor (mg NO$_3$–N·mg X_a^{-1}·h^{-1})
K_a = specific adsorption rate constant (l mg X_a^{-1}·d^{-1})
K_m = maximum specific utilization constant (mg COD·mg X_a^{-1}·d^{-1})
K_n = Monod half saturation concentration for nitrification (mg NH$_3$–N·l^{-1})
K_s = Monod half saturation concentration for biodegradable organic material (mg COD·l^{-1})
N_a = ammonia concentration (mg N·l^{-1})
N_n = nitrate concentration (mg N·l^{-1})
O_c = oxygen uptake rate for carbonaceous energy removal (mg O·l^{-1}·h^{-1})
O_n = oxygen uptake rate for nitrification (mg O·l^{-1}·h^{-1})
O_t = total oxygen uptake rate (mg O·l^{-1}·h^{-1})
P = COD/VSS ratio (mg COD·mg VSS^{-1})
R = nominal reactor retention time (h or d)
R_a = actual retention time (h or d)
R_h = hydraulic retention time (h or d)
R_s = sludge age (d)
S = general parameter for COD concentration (mg COD·l^{-1})
S_b = biodegradable COD concentration (mg COD·l^{-1})
S_t = total COD concentration (mg COD·l^{-1})
T = temperature
X = general parameter for sludge concentration (mg VSS·l^{-1})
X_a = active sludge concentration (mg VSS·l^{-1})
X_e = concentration of endogenous residue (mg VSS·l^{-1})
X_n = concentration of nitrifiers (mg VSS·l^{-1})
X_s = concentration of stored material (mg VSS·l^{-1})
Y_h = yield coefficient for heterotrophs (mg VSS·mg COD^{-1})
Y_n = yield coefficient for nitrifiers (mg X_n·mg NH$_3$–N^{-1})
α = proportionality constant
ΔN = nitrogen requirement for sludge synthesis (mg N·l^{-1})
ΔN_a = reactor nitrate removal (mg NO$_3$–N·l^{-1})
ΔN_s = system nitrate removal (mg NO$_3$–N·l^{-1})
μ_{nm} = maximum specific growth rate of nitrifiers (mg X_n·mg X_n^{-1}·d^{-1})
θ = Arrhenius temperature dependency coefficient

Additional indexes:

p = refers to slowly biodegradable material
s = refers to easily biodegradable material
T = refers to temperature
1 = refers to pre-denitrification
3 = refers to post-denitrification
' = refers to an aerobic environment
" = refers to an anoxic environment
i = refers to influent

INTRODUCTION

In the single sludge nitrification–denitrification process organic material in the influent is utilized as electron donor in the denitrification reaction. Procedures for determining the mass of nitrogen removed have been, in the main, empirically based. One approach has been to model the observed denitrification response as one additional to and largely independent of the aerobic response—the aerobic phase produces the volatile mass which in turn is accepted as the basic parameter in formulating the denitrification phase. Under constant flow and load conditions development of this approach has resulted in a remarkable close description of the denitrification behaviour. However when flow and load varies daily cyclically this empirical approach has failed completely—an approach taking cognisance of the basic kinetics governing the system is needed.

Modelling of nitrification–denitrification systems has been limited to the 3 and 2 sludge systems. In the 3 sludge system complete separation of the respective carbonaceous energy removal, nitrification and denitrification phases is achieved by having 3 separate reactor systems with settlers in series, 1 for each phase. In the 2 sludge system the energy removal and nitrification phases take place in 1 reactor and that of denitrification in a second. Modelling of energy removal and nitrification in one reactor has not presented any serious difficulties, the reason for this is that the 2 reactions are mediated by two entirely different groups of organisms—the auto-trophic nitrifiers and heterotrophic energy removers. Their respective kinetic behaviour can be modelled virtually independently of each other; the process response of the two are linked only insofar as the reactor and the process parameters (sludge age, temperature) are common to both, and that ammonia is abstracted from the wastewater for growth by both groups of organisms.

In both the 3 and 2 sludge systems the denitrification phase is entirely divorced from the preceding energy removal and nitrification phases. The only common feature is the nitrate in the effluent/influent flow link. The denitrification reactor develops its own sludge mass under very specific conditions—a simple soluble easily biodegradable energy source is added to the reactor in which nitrate is the sole electron acceptor. Consequently, the denitrification reactor organism mass also is very specific. The denitrification process in the denitrification reactor has been successfully modelled by Stensel *et al.* (1973) on lines very similar to the activated sludge model of Lawrence & McCarty (1970).

In the single sludge process the same mass of sludge accomplishes aerobic energy removal, nitrification and denitrification. Nitrification and denitrification is achieved either by imposing sequentially anoxic and aerobic conditions on the mixed liquor in a single reactor, or, by having a minimum of 2 reactors of which one is maintained anoxic and the other aerobic and recycling the sludge between the 2 reactors.

Modelling of the single sludge process requires description of a complex system of intereacting reactions: energy removal for heterotrophic growth takes place from the same substrate source under both aerobic and anoxic (denitrification) conditions by the same organism mass, i.e. the same organism mass must react alternately to oxygen and nitrate as electron acceptors; nitrification is affected by anoxic conditions in that growth of nitrifiers can take place only in an aerobic environment, but endogenous respiration takes place under both aerobic and anoxic conditions. The main problem area however is the behaviour of the heterotrophic organisms under alternating anoxic and aerobic conditions. Despite the complexity of the behaviour of the single sludge nitrification–denitrification process, because denitrification, like aerobic energy removal, is mediated by heterotrophic facultative organisms, one can hypothesise that modelling of their respective behaviour under sequential aerobic–anoxic conditions should not be qualitatively dissimilar even though quantitatively their response may differ. In this paper it will be shown that in the single sludge nitrification–denitrification process when the organisms are in the anoxic phase it is necessary to change the value of only one of the kinetic constants in order to model the nitrification–denitrification single sludge system in terms of the bi-substrate active-site death-regeneration model of Dold *et al.* (1980).

NITROGEN REMOVAL IN THE ACTIVATED SLUDGE PROCESS

In municipal wastewaters nitrogen is present principally in the form of amino compounds (organic nitrogen) and ammonia. In the activated sludge process nitrogen is removed wholly or partially from the wastewater by biological activities of the microorganisms, through (1) incorporation into the sludge, and (2) reduction of nitrate (or nitrite) to nitrogen gas when nitrate (or nitrite) serves as electron acceptor.

Nitrogen incorporation into the sludge mass

Fractions of the influent nitrogen mass are removed by incorporation into the active bio-mass, endogenous residue mass generated, and inert organic particulate mass in the influent enmeshed in the sludge mass, respectively. In terms of the synthesis-endogenous respiration kinetic theory for the activated sludge pro-

cess, Marais & Ekama (1976) developed the following equation to determine the concentration of nitrogen removed from the influent flow under constant flow and load conditions:

$$\Delta N = f_n \cdot \left[\frac{Y_h(1 + f \cdot b_{hT} \cdot R_s)}{1 + b_{hT} \cdot R_s} \times (1 - f_{us} - P \cdot f_{up}) + f_{up} \right] S_{ti}. \quad (1)$$

From equation (1), for sludge ages longer than 10 days the concentration of influent nitrogen removed per mg influent COD ($\Delta N/S_{ti}$) is less than 0.03. Raw domestic sewage generally has a TKN/S_{ti} ratio of 0.07–0.10; it follows that only a minor part of the influent nitrogen is removed by incorporation in the sludge (20–30%).

Nitrogen removal by reduction of nitrate

This biochemical reaction is known as dissimilative reduction of nitrogen or denitrification and involves the reduction of nitrate or nitrite, present in the wastewater, to gaseous nitrogen which escapes to the atmosphere. The removal of nitrogen is a consequence of biological redox reactions wherein biodegradable organic material serves as electron donor and nitrate or nitrite serves the same function as oxygen, i.e. as electron acceptor. The equivalence is evident in the following half-reactions:

Oxygen

$$e^- + \tfrac{1}{4}O_2 + H^+ \rightarrow \tfrac{1}{2}H_2O \quad (2)$$

Nitrate

$$e^- + \tfrac{1}{5}NO_3^- + \tfrac{6}{5}H^+ \rightarrow \tfrac{1}{10}N_2 + \tfrac{3}{5}H_2O \quad (3)$$

Nitrite

$$e^- + \tfrac{1}{3}NO_2^- + \tfrac{4}{3}H^+ \rightarrow \tfrac{1}{6}N_2 + H_2O. \quad (4)$$

In transferring electrons from the organic material to the electron acceptor (oxygen, nitrate or nitrite) there are approximately equal changes of free energy per electron transferred irrespective of the donor or acceptor (McCarty, 1964)*. From equations (2) and (3) it can be noted that the transfer of 1 electron equivalent involves the reduction of $\frac{1}{4}$ mol of oxygen, or $\frac{1}{5}$ mol of nitrate, i.e. $\frac{32}{4}$ g $O_2 \equiv \frac{14}{5}$ g NO_3–N, or, 1 mg NO_3–N $\equiv$ 2.86 mg O_2 (or COD). Nitrite usually is present only in insignificant amounts in nitrification–denitrification systems and will not be considered further.

Nitrate readily replaces oxygen as electron acceptor because the pathway for the transfer of electrons from the organic substrate to the final electron acceptor is similar (Christensen & Harremoës, 1972), but the presence of dissolved oxygen acts as a strong inhibitor on denitrification as it prevents the formation of the enzyme necessary for the final electron transfer to nitrate (Chong & Morris, 1962).

From the above it can be concluded that there are 4 conditions that are necessary for denitrification:

1. Presence of nitrate
2. Absence of dissolved oxygen
3. Bacterial mass that can accept nitrate and oxygen as electron acceptor
4. Presence of a suitable electron donor (energy source).

With regard to (1), in the treatment of municipal wastes, the presence of nitrate implies that nitrification is a prerequisite for denitrification. With regard to (2) and (3), an environment that satisfies both is called anoxic†. With regard to (3), the ability to denitrify is widespread among bacteria; dissimilative denitrification with end products N_2, NO and NO_2 has been established in numerous cases (Christensen & Harremoës, 1977). The bulk of the bacterial mass in wastewater treatment systems is facultative and a significant fraction is capable of dissimilative denitrification. With regard to (4), a variety of carbonaceous organic substances have been investigated as energy sources for denitrification; these can be categorized as follows:

(a) Energy source not present in wastewater, i.e. an external carbonaceous energy source (e.g. methanol).

(b) Energy source present in the influent wastewater, i.e. internal (influent) energy source.

(c) Energy source generated within the system by the release of substrate by organisms death and lysis, i.e. self-generated energy source.

The external energy source is associated with the 2 and 3 sludge systems, wherein the energy source is added at the denitrification stage. Internal and self-generated energy sources are associated with the single sludge nitrification–denitrification system, wherein the same biological mass is placed alternately in anoxic and aerobic environments. Only the single sludge nitrification–denitrification system will be discussed in this paper.

Process configurations

There are two basic configurations for the single sludge nitrification–denitrification system depending on the type of energy source, i.e. (1) internal or (2) self-generated.

(1) *Internal (influent) energy source.* Ludzack & Ettinger (1962) were first to propose a process configuration utilizing the biodegradable material in the influent as the main energy source for denitrification. Their configuration is given in Fig. 1(a). The anoxic reactor is in partial communication with the aerobic

* This is the basis of the COD test as a means for estimating free energy change in terms of oxygen.

† An environment wherein neither oxygen nor nitrate is present is called anaerobic. Differentiation between anoxic and anaerobic states is necessary because the establishment of an anaerobic state is one of the necessary (but not sufficient) prerequisites for inducing excess biological uptake of phosphorus.

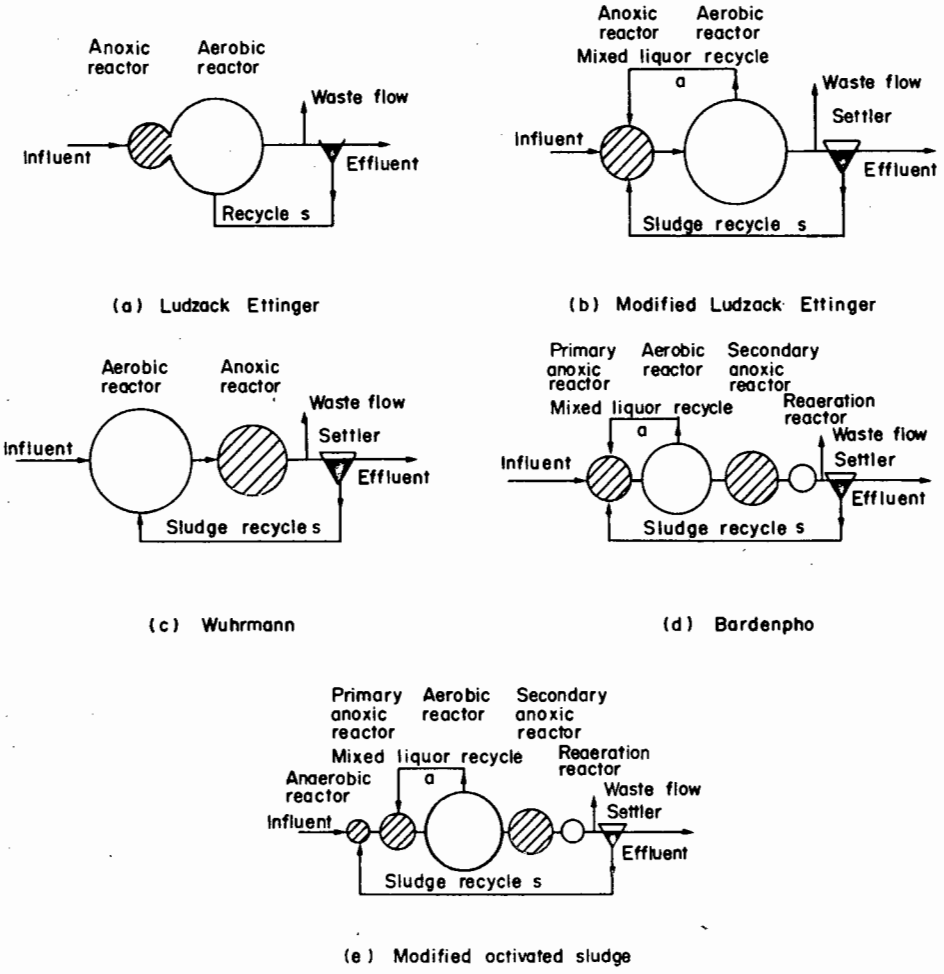


Fig. 1. Single sludge nitrification–denitrification activated sludge process configurations. (a) Ludzack Ettinger; (b) Modified Ludzack Ettinger; (c) Wuhrmann; (d) Bardenpho; (e) Modified activated sludge.

reactor. The influent is discharged to the anoxic reactor and the underflow recycle from the settling tank is discharged to the aerobic reactor. Nitrification takes place in the aerobic reactor and nitrified mixed liquor is cycled to the anoxic reactor in a rather indeterminate fashion by the mixing action in the two reactors. As a consequence the denitrification performance of the process is very variable.

Barnard (1973) in developing the Bardenpho system proposed (1) complete separation of the anoxic reactor (also called the pre-denitrification reactor), and (2) the introduction of controlled recycle from the aerobic to the anoxic reactor and (3) discharge of the underflow recycle to the anoxic reactor (Fig. 1b). We can apply this modification to the Ludzack–Ettinger system and for identification call the process the Modified Ludzack–Ettinger (MLE) process. Compared with the original process the modified process has given improved and more consistent performance.

The MLE process cannot reduce the effluent nitrate concentration to zero because the net concentration of nitrate established in the aerobic reactor (under the concentrations generated in that reactor and removed by the denitrification recycles) is the source for both the recycle and the effluent flows.

(2) *Self-generated energy source.* The nitrification–denitrification configuration in which endogenous death and lysis provides the energy for denitrification was first proposed by Wuhrmann (1964). A schematic representation of this process is shown in Fig. 1(c). The first reactor, which is aerobic, receives the influent flow and sludge return flow from the settling tank; nitrification of the influent TKN occurs in this reactor. The contents of the aerobic reactor discharge to the anoxic reactor (also called the post-denitrification reactor) where denitrification takes place.

The rate of energy release due to organism death and lysis is low, resulting in a low rate of denitrification. Hence a high degree of denitrification requires a large anoxic sludge mass fraction, but experience has shown that this may affect the nitrification efficiency of the process: the nitrifiers are obligate aerobes, consequently they can multiply only in the aerobic zone of the process. If the organism retention time in the aerobic zone is too short, the nitrifiers cannot reproduce and nitrification ceases. Therefore, in a design it

is possible that, in order to obtain complete denitrification, the required anoxic sludge fraction is so great that nitrification does not take place. Usually for any sludge age the nitrification requirement places a lower limit on the aerobic mass fraction and thereby, an upper limit on the anoxic sludge mass fraction; the latter in turn places a limit on the mass of nitrate that can be denitrified.

The two basic configurations described above have been combined to (a) obtain higher denitrification efficiencies, or (b) create conditions necessary for luxury uptake of phosphorus.

(a) Barnard (1973) proposed combining the MLE and Wuhrmann configurations to obtain a low nitrate in the effluent, called the Bardenpho process (see Fig. 1d). He added a flash aeration reactor before the final settling tank to strip nitrogen gas bubbles from the flocs and to nitrify ammonia released in the post-denitrification reactor.

(b) In 1976 Barnard noted that enhanced biological phosphorus removal is induced if, at some point in the process, the mixed liquor is maintained in an anaerobic condition such that phosphorus is released from the organism mass. To obtain this condition efficiently an "anaerobic reactor" was included ahead of the pre-denitrification reactor to receive the influent and the underflow recycle (see Fig. 1e). Due to the relatively low mass of nitrate in the underflow recycle it was hypothesized that the capacity for denitrification of the anaerobic reactor will be greater than the mass of nitrate introduced and hence anaerobic conditions sufficient to cause release of phosphorus will be assured. This configuration is called the Phoredox system.

The design of these processes has been largely empirical, based on pilot plant behaviour. The problem with this approach is that, because the basic mechanisms are not quantitatively delineated, it is almost impossible to predict the denitrification behaviour once the temperatures, sludge ages or sewage characteristics differ from those in the pilot plant investigation. For this reason a wide-ranging experimental investigation was initiated to enquire if there is a basic pattern of behaviour that does allow a general design approach.

EXPERIMENTALLY BASED DENITRIFICATION MODEL

Carlson (1971) and Christensen & Harremoes (1972) suggested that the kinetic reaction describing denitrification by the activated sludge mixed liquor can be expressed by:

$$dN/dt = -KX_v \quad (5)$$

where

N = nitrate concentration, mg $(NO_3\text{–}N)\cdot l^{-1}$
(dN/dt) = denitrification rate, mg $N\cdot l^{-1}\cdot time^{-1}$
t = time in hours or days
X_v = volatile solids concentration, mg $\cdot l^{-1}$
K = specific denitrification constant, mg $N\cdot$ mg $VSS^{-1}\cdot time^{-1}$.

Equation (5) was developed from batch tests. It indicates that the nitrate–time relationship is linear and independent of the nitrate concentration, i.e. the denitrification rate is a zero order reaction with respect to the nitrate concentration, and a function only of the volatile solids concentration. Although the denitrification reaction may exhibit zero order characteristics in batch tests such a relationship does not signify a basic biological relationship. When batch experiments are done with aerobic sludge, linear oxygen time profiles are always obtained and can be described by a relationship such as equation (5), but an activated sludge theory cannot be developed only from such a behavioural pattern, as it is the consequence of a number of mechanisms operating in the process. However, it is possible that in a multi-reactor nitrification–denitrification system, the reaction in the anoxic reactors may exhibit characteristics that can be modelled empirically by a linear relationship such as equation (5). If, for example, K in equation (5) shows reasonable constancy and is independent of the influent COD in different nitrification–denitrification configurations, it would serve adequately as a design tool even though it is empirical.

Experimental background

In order to evaluate equation (5) as a basis for describing denitrification behaviour, Marais and a number of co-workers (Stern & Marais, 1974; Wilson & Marais, 1976; Marsden & Marais, 1976) undertook an extensive investigation into the kinetic behaviour of the Modified Ludzack–Ettinger and Wuhrmann systems using plug-flow régimes for the respective anoxic reactors. By sampling the nitrate concentration along the length of an anoxic plug-flow reactor the denitrification kinetic behaviour could be determined by plotting time profiles of the nitrate concentration. Experiments were carried out using only raw and settled municipal influents, over a range of sludge ages, sludge concentrations, influent COD concentrations and recycle ratios between 14 and 20 C.

Under constant flow and load conditions the nitrate concentration-retention time profiles typically exhibited shapes as indicated in Fig. 2(a) and 2(b) for pre- and post-denitrification reactors respectively. The post-denitrification profiles all exhibited a single phase linear decrease of the nitrate concentration with time, i.e. behaviour that can be described by equation (5). The pre-denitrification profiles however, all indicated a two phase denitrification response, i.e. (1) a fast primary phase of short duration (1–9 min) followed by (2) a slower secondary phase that persisted for the balance of the time in the plug-flow reactor.

Analysis of the experimental data over a range of sludge ages (10–20 days) indicated that the rate of denitrification was directly proportional to the concentration of the active fraction of the sludge, X_a, not to the total volatile sludge concentration, X_v, as suggested by Christensen & Harremoes (1972). The concentration X_a was estimated utilizing the equation proposed by Marais & Ekama (1976) (based on the systhesis-endogenous respiration approach to activated sludge kinetics) for constant flow and load conditions, i.e.

$$X_a = \frac{Y_h S_{bi}}{1 + b_{hT} R_s} \cdot \frac{R_s}{R_b} \quad (6)^*$$

where

$$b_{hT} = 0.24(1.029)^{T-20}.$$

* At all sludge ages >4 days under constant flow and load conditions the concentration of active sludge, X_a, given by equation (6) (endogenous-respiration approach) is virtually identical to the value calculated from the death-regeneration approach of Dold *et al.* (1980). The reason for this is that the two approaches are linearly related and give the same response once the stored biodegradable and easily biodegradable COD concentrations are negligible.

With regard to the applicability of equation (6) to anoxic–aerobic systems, experimental data indicate that, provided the anoxic volume fraction is less than 40%, the production of sludge does not appear to be significantly different from that generated in a completely aerobic system (Stern & Marais, 1974; Heide, 1977). One can infer from this that both Y_h and b_{hT} are not significantly affected by the anoxic zone (when it is not too large) and, that organism death and lysis takes place in both the aerobic and anoxic zones.

Experimentally based model

In a plug-flow reactor in a nitrification–denitrification system, if the rate of denitrification is constant over the actual hydraulic retention time of the anoxic reactor, R_a, a denitrification rate constant can be defined by equation (5), except that X_a replaces X_v, i.e.

$$K = \Delta N_a/(R_a X_a) \tag{7}$$

where

ΔN_a = difference between influent and effluent nitrate concentrations ($N_i - N_e$) in the plug-flow reactor.

If the rate of flow through the plug-flow reactor is $Q\cdot(1 + a)$ (where Q = average influent flow rate to the plant and a = recycle ratio) the flow passes $(a + 1)$ times through the reactor and the system removal ΔN_s is given by:

$$\Delta N_s = (a + 1)\cdot\Delta N_a = (a + 1)(N_i - N_e). \tag{8}$$

The nominal retention time R is defined by V/reactor)/Q and is related to the actual retention time, R_a, by

$$R = R_a(a + 1). \tag{9}$$

Substituting equations (8) and (9) in equation (7):

$$\begin{aligned} K &= \Delta N_s/(RX_a) \\ &= \Delta N_a(1 + a)/(R_a(1 + a)X_a) \\ &= \Delta N_a/(R_a X_a). \end{aligned} \tag{10}$$

Equations (7)–(9) are valid only if the nitrate is not reduced to zero somewhere before the end of the plug-flow reactor flow path. From the development of equation (10) [from equation (7)], it is evident that K is independent of the recycle ratio, a.

Considering the plug-flow post-denitrification reactor, (Fig. 2a), the conditions are identical to those stated for the formulation of equation (7) (Fig. 2b). Consequently, the system removal of nitrate, ΔN_{3s}, can be written directly,

$$\Delta N_{3s} = K_3 X_a R_3 \tag{11}$$

where the index 3 refers to the post-denitrification reactor.

* The value of K_3 at 20°C was determined in a completely mixed reactor.

Considering the pre-denitrification reactor (Fig. 2), equation (7) cannot be applied directly. In this reactor two rate phases are observed (Fig. 2a). In order to determine a denitrification rate constant for each phase, it was assumed that in the first phase the high rate is due to two simultaneous processes: a primary rate with a denitrification rate constant, K_1, that persists only over the period of the primary phase, t_p, and a secondary rate with a denitrification rate constant, K_2, that persists for the total time in the anoxic reactor (interrupted lines in Fig. 2a). (Later it will become evident that there is good reason for this assumption.) Consequently, the system removal ΔN_s can be expressed as:

$$\begin{aligned} \Delta N_s &= \Delta N_{1s} + \Delta N_{2s} \\ &= K_1 X_a\cdot t_p(a + 1) + K_2 X_a R_1 \end{aligned} \tag{12}$$

where

ΔN_{1s} = system removal due to denitrification with rate constant K_1

ΔN_{2s} = system removal due to denitrification with rate constant K_2

R_1 = nominal retention time in the pre-denitrification reactor

t_p = duration of the primary phase in h.

From numerous experimental nitrate profiles the values of K_1, K_2 and K_3 were calculated over a range of sludge ages, from 10 to 20 days, temperatures from 14 to 20°C and influent COD's from 300 to 800 mg l^{-1}. Figure 3(a) shows a statistical plot for both K_1 and K_2 at 14 and 20°C respectively, and Fig. 3(b) a plot for K_3 at 14°C (R_s = 20 days).

Statistical comparisons of the respective mean K_1, K_2 and K_3 values at the same temperature, but at different sludge ages for different influent COD concentrations, showed not significant differences, i.e. the K values appeared to be independent of sludge age, influent COD, sludge concentration and recycle ratios.

Temperature dependency of the mean K_1, K_2 and K_3 values respectively was formulated assuming an Arrhenius type equation:

$$K_{1T} = 0.03(1.20)^{T-20}\ \text{mg N}\cdot\text{mg}\ X_a^{-1}\cdot\text{h}^{-1} \tag{13}$$

$$K_{2T} = 0.0042(1.08)^{T-20}\ \text{mg N}\cdot\text{mg}\ X_a^{-1}\cdot\text{h}^{-1} \tag{14}$$

$$K_{3T} = 0.0033(1.03)^{T-20}\ \text{mg N}\cdot\text{mg}\ X_a^{-1}\cdot\text{h}^{-1}.* \tag{15}$$

The system reduction of nitrate, ΔN_{1s}, due to the reaction with rate constant, K_1, was also calculated. It was found that ΔN_{1s} is proportional to the influent biodegradable COD concentration and independent of the temperature, sludge concentration and recycle ratio (Stern & Marais, 1974).

Hence ΔN_{1s} can be formulated as

$$\Delta N_{1s} = \alpha S_{bi}. \tag{16}$$

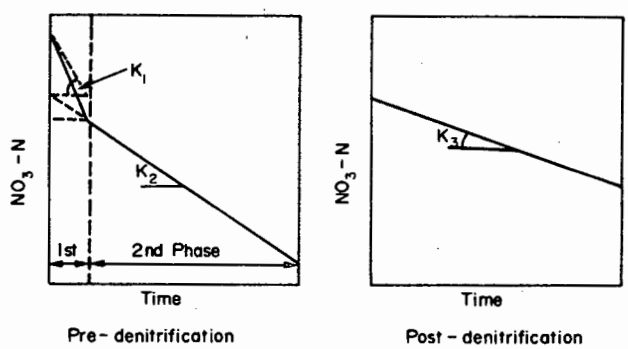


Fig. 2. Typical nitrate concentration–retention time profiles in anoxic plug flow reactors.

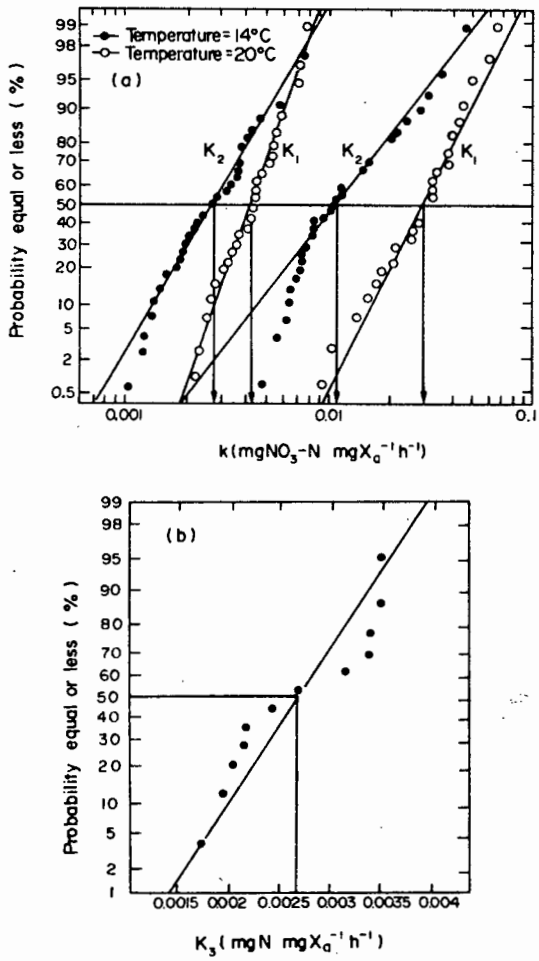


Fig. 3. (a) Statistical plot of the denitrification rate constants K_1 and K_2 in a pre-denitrification reactor. (b) Statistical plot of the denitrification rate constant K_3 in a post-denitrification reactor.

The mean experimental value of α was found to be 0.028 mg N·mg S_{bi}^{-1}. (See Fig. 4.)

The values of K_1, K_2 and K_3 and in equations (13)–(16) are mean values. The data showed wide variation (see Fig. 3) and although the standard deviation of the mean is small, it should not be inferred that the mean has a corresponding stability: reviewing the data indicates that sequences of low and high values were often obtained. The lengths of these sequences were usually associated with the feed periods of a batch of influent sewage (one batch was used for 1–2 weeks). Variation of $\pm 25\%$ in the values of K_1, K_2, K_3 and α were not uncommon. The changes in these values very evidently were in part due to changes in the sewage characteristics from batch to batch. Identification of some of the causes of change will become possible after modelling the general behaviour of the process later in this paper.

The fact that linear nitrate profiles are obtained in plug-flow reactors indicates that in the particular states present in these reactors the denitrification rate approximates a zero order reaction. Consequently if completely mixed reactors replace the plug flow reactors the nitrogen removal again should be amenable to estimation by means of the equations developed above, all of which implicitly contain the zero order approximation. In experiments where the plug flow reactors were replaced by completely mixed reactors it was found repeatedly that within experimental error, the denitrification achieved in the completely mixed reactors was in accordance with the predictions of equations (7)–(17) using the experimentally determined values for K_1, K_2 and K_3 [equations (13)–(15)], and α [equation (16)].

The system reduction for a process having both pre- and post-denitrification reactors (Fig. 1d) can now be written:

$$\Delta N_s = \Delta N_{1s} + \Delta N_{2s} + \Delta N_{3s} = \alpha S_{bi} + K_2 X_a R_1 + K_3 X_a R_3. \quad (17)$$

An important point to note is that equation (17) is valid only if the nitrate is not reduced to zero in any one of the anoxic reactors. If this condition is satisfied the recycle ratio does not affect the system reduction. However, there must be a minimum recycle; this is determined by the recycle value that just causes the nitrate to be zero at the end of the plug flow reactor. If the recycle is less, the nitrate will become zero before the end of the reactor is reached—the recycle can be increased (with concomitant increase in the nitrate removal) to the point where nitrate just starts to appear in the effluent. Once nitrate appears in the effluent from all the anoxic reactors then theoretically, a further increase in the recycle will have no effect on the system nitrate reduction. Practically, however, it is necessary to take into account the oxygen in the recycles; at high recycles the mass of oxygen introduced may significantly reduce the mass of nitrate denitrified in an anoxic reactor.

Essentially the relationships developed above are empirical; except for the linkage of denitrification with X_a instead of X_v, there is no evident link with the activated sludge process theory. To find such a link attention was directed to the general theory for aerobic processes developed by Dold *et al.* (1980).

INTEGRATION WITH THE GENERAL THEORY

In the general theory by Dold *et al.* (1980) it is stated that the biodegradable material in municipal sewage expressed as COD is divided into two fractions, (a) easily biodegradable (about 24% of the total biodegradable COD), and (b) particulate slowly bio-

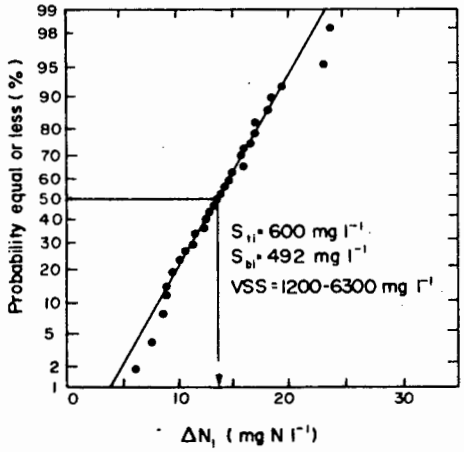


Fig. 4. Statistical plot of the system nitrate removal due to high rate denitrification.

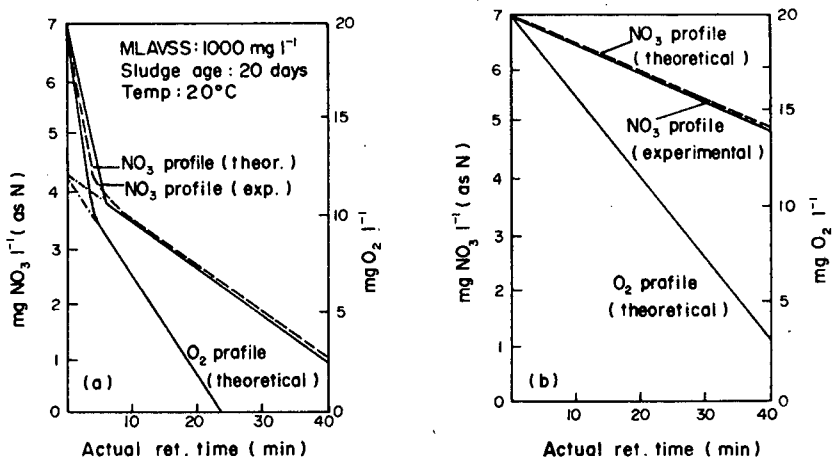


Fig. 5. Experimental and simulated NO_3-time profiles in an anoxic plug flow reactor and DO-time profile in an aerobic plug flow reactor.

degradable (76%).* To incorporate denitrification kinetics into the aerobic kinetic model it was hypothesized that the two phase behaviour observed in the pre-denitrification reactor arose from the response of the organisms to the two substrate character of the influent feed. If this is correct, then theoretically the two phase behaviour should be predicted also if the plug-flow anoxic reactors are replaced by plug-flow aerobic reactors, and the process operated under constant load and flow conditions. Accordingly, plug-flow reactor options were incorporated into the general aerobic model, and under constant load and flow conditions oxygen profiles for the pre- and post-aerobic reactors were generated.

The simulated response of the dissolved oxygen profile in the pre- and post-aerobic plug-flow reactors for $X_a = 1000 \cdot 1^{-1}$, sludge age = 20 d, temperature = 20°C is shown in Fig. 5(a) and (b) respectively. Also shown are the nitrate profiles based on the experimental values of the denitrification rate constants and α [equations (13)–(16)] and plotted as equivalent oxygen†, to allow direct comparison between the respective curves. The simulated aerobic and observed anoxic profiles are strikingly similar: the two phase behaviour in the pre-anoxic reactor and the single phase behaviour in the post-anoxic reactor, is clearly reproduced in the aerobic simulations, except that the simulated slopes corresponding to the K_2 and K_3 rate phases differ from the observed anoxic slopes. Furthermore, the concentration of nitrate (or equivalent oxygen) removed due to the high rate in the primary phase of the anoxic reactor is the same as the corresponding concentration of oxygen removed in the aerobic reactor (see extrapolation to $t = 0$ in Fig. 5a). The similarity of the profiles is so clearly evident that it was accepted that the general aerobic model can provide a basis for modelling the denitrification behaviour. The problem now was what changes and additions needed to be made to the aerobic model to allow a quantitative description of the response of a nitrification–denitrification single sludge system. The following aspects formed the basis for formulating the changes necessary.

1. In the bi-substrate active-site death-regeneration model there is only growth (synthesis) and death, the latter with its associated substrate release by lysis; no endogenous respiration *per se*, is recognized. From comparisons of the oxygen utilization rates in completely mixed reactors, simulated and observed, in different aerobic systems, it appears that the lysed material is slowly biodegradable particulate COD. This material is added to the same material derived from the influent to constitute the energy source of slowly biodegradable particulate material [equation (23)].

2. Growth of the heterotrophs is assumed to take place in both aerobic and anoxic conditions; death and lysis take place irrespective of whether the conditions are aerobic, anoxic or anaerobic. Under anaerobic conditions no heterotrophic growth can take place, but, due to death and lysis there is a corresponding accumulation of lysed slowly biodegradable material.

3. Growth of the nitrifiers can take place only under aerobic conditions; death is assumed to take place irrespective of aerobic, anoxic or anaerobic conditions.

4. The general theory accepts that easily biodegradable and slowly biodegradable material are simultaneously and independently utilized in synthesis [equations (22) and (24)]. This assumption is reasonable, unless the particulate material stored on the active sites are all occupied (a situation possible in the contact reactor of a contact stabilization plant).

* The composition of COD in municipal sewage is approximately as follows: 5% soluble unbiodegradable; 13% particulate unbiodegradable; 20% easily biodegradable and 62% particulate biodegradable.

† Adjustment on the basis of 1 mg NO_3–N ≡ 2.86 mg O_2.

Normally the organisms remain essentially in a continuous state of stress due to the low food/microorganism ratio even under cyclic loading conditions, once the sludge age exceeds 4–6 days.

For the general model the differential equations describing the aerobic system have been set out by Dold *et al.* (1980) and for convenience, are repeated here.

Let

$$A = K_{ms} \cdot S_{bs}/(S_{bs} + K_{ss}) \quad (18)$$

$$B = K_a S_{bp} \cdot (f_{ma} - X_s/X_a) \quad (19)$$

$$C = K'_{mp} \cdot \mathrm{P} \cdot X_s/(X_s \mathrm{P} + K_{sp} X_a) \quad (20)$$

$$D = \mathrm{P} \cdot b'_h. \quad (21)$$

Then the differential equations for energy removal are:

$$dS_{bs}/dt = -A \cdot X_a \quad (22)$$

$$dS_{bp}/dt = (-B + (1 - f')D) \cdot X_a \quad (23)$$

$$dX_s/dt = (B - C)/\mathrm{P} \cdot X_a \quad (24)$$

$$dX_a/dt = (Y_h(A + C) - D/\mathrm{P})X_a \quad (25)$$

$$dX_e/dt = f'\mathrm{D}/\mathrm{P} \cdot X_a \quad (26)$$

$$O_e = (1 - \mathrm{P}Y_h)(A + C)X_a. \quad (27)$$

Let

$$E = \mu_{nm}/Y_n \cdot N_a/(N_a + K_n) \quad (28)$$

$$F = b_n. \quad (29)$$

Then the differential equations for nitrification are:

$$dN_a/dt = -E \cdot X_n \quad (30)$$

$$dN_n/dt = EX_n \quad (31)$$

$$dX_n/dt = (Y_n E - F) \cdot X_n \quad (32)$$

$$O_n = 4.57\, E \cdot X_n. \quad (33)$$

The temperature dependency of the various constants are:

(a) Carbonaceous (energy removal)

$$K_{ms} = 8(1.20)^{T-20}\ \mathrm{mg\ COD \cdot mg\ VASS^{-1} \cdot d^{-1}} \quad (34)$$

$$K_{ss} = 5(1.00)^{T-20}\ \mathrm{mg\ COD \cdot l^{-1}} \quad (35)$$

$$K'_{mp} = 3.0(1.060)^{T-20}\ \mathrm{mg\ COD \cdot mg\ VASS^{-1} \cdot d^{-1}} \quad (36)$$

$$K'_{sp} = 0.04(1.1)^{20-T}\ \mathrm{mg\ COD \cdot mg\ VASS^{-1}} \quad (37)$$

$$K_a = 0.25(1.029)^{T-20}\ \mathrm{l \cdot mg\ VSS^{-1} \cdot d^{-1}} \quad (38)$$

$$b'_h = 0.62(1.029)^{T-20}\ \mathrm{mg\ VASS \cdot mg\ VASS^{-1} \cdot d^{-1}} \quad (39)$$

$$f' = 0.08\ \mathrm{mg\ VSS \cdot mg\ VASS^{-1}} \quad (40)$$

$$\mathrm{P} = 1.48\ \mathrm{mg\ COD \cdot mg\ VSS^{-1}} \quad (41)$$

$$Y_h = 0.45\ \mathrm{mg\ VSS \cdot mg\ COD^{-1}}. \quad (42)$$

(b) Nitrogeneous (nitrification)

$$\mu_{nm} = (0.3\text{–}0.65)(1.123)^{T-20}\ 7.2 \leqslant \mathrm{pH} \leqslant 8.0 \quad (43)$$

$$b_n = 0.04(1.029)^{T-20}\ \mathrm{mg}\ X_n \cdot \mathrm{mg}\ X_n^{-1} \cdot \mathrm{d}^{-1} \quad (44)$$

$$Y_n = 0.1\ \mathrm{mg}\ X_n \cdot \mathrm{mg\ NH_3\text{–}N^{-1}}. \quad (45)$$

Equation (27) describes the oxygen utilization rate and needs adjustment for an anoxic environment in order to express the utilization rate of nitrate instead of oxygen:

$$(dN_n/dt) = -(1 - \mathrm{P}Y_h)(A + C) \cdot X_a/2.86. \quad (46)$$

The fact that the observed rate of nitrate removal (as equivalent oxygen) in the anoxic reactors was not so rapid as the simulated decrease of dissolved oxygen in the aerobic reactors (Fig. 5a and b) indicated that the rate of utilization of particulate substrate in the anoxic environment is lower. The degree in which the rate is reduced was estimated by considering first the post-denitrification reactor.

In the post-denitrification reactor the concentration of easily biodegradable nutrient is virtually zero and the rate of nitrate removal is associated only with the utilization of slowly biodegradable material. It was possible to simulate the experimental nitrate profile in a post-denitrification reactor at 20 C accurately when the value of the maximum specific substrate utilization rate constant, K'_{mp}, for slowly biodegradable material was reduced to a fraction, 0.38, of the value this constant has in an aerobic environment. Figure 5(b) shows the simulated nitrate profile in a post-denitrification plug-flow reactor for $T = 20$ C, $R_s = 20$ d, $X_a = 1000\ \mathrm{mg \cdot l^{-1}}$ and an anoxic sludge fraction of 25%, when the maximum specific substrate utilization rate for slowly biodegradable substrate, K''_{mp}, is set at a value:

$$K''_{mp} = 0.38\, K'_{mp} = 1.14\ \mathrm{mg\ COD \cdot mg}\ X_a^{-1} \cdot \mathrm{d^{-1}}\ (\text{at } 20\ \mathrm{C}). \quad (47)$$

When this same value for K''_{mp} was used to simulate denitrification in a pre-denitrification reactor under the same conditions of temperature, sludge age and anoxic volume fraction, again a very close correspondence between simulated and experimental nitrate profiles in the secondary phase was obtained (see Fig. 5a).

With regard to the maximum specific utilization rate constant for easily biodegradable material, Dold *et al.* (1980) could not determine K_{ms} accurately in an aerobic environment from the completely mixed reactor response under square wave cyclic flow and load conditions. The utilization of easily biodegradable substrate is an extremely rapid reaction and all that could be established was a lower limit for the constant—any value greater than the minimum, predicted a behaviour in conformity with the observation. The lower limit was determined as $K_{ms} = 5\ \mathrm{mg\ COD \cdot mg}\ X_a^{-1} \mathrm{d^{-1}}$ at 20 C. However, in anoxic plug flow reactors it was possible to derive a value for

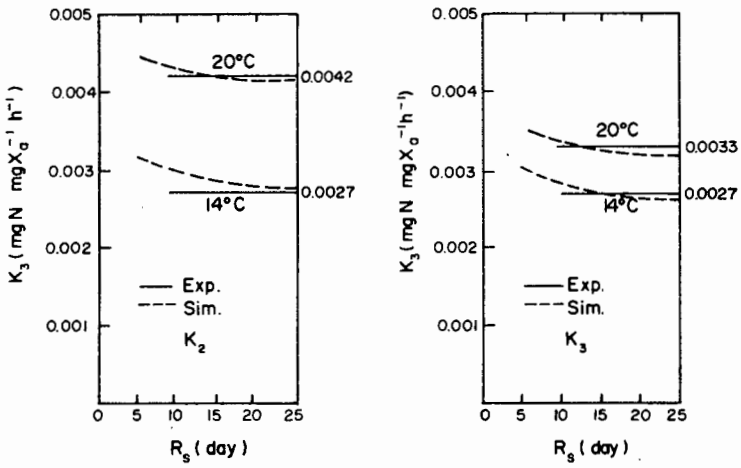


Fig. 6. Simulated and experimental denitrification rate constants K_2 (a) and K_3 (b) vs sludge age.

K_{ms} from fitting simulated and experimental nitrate profiles in the plug flow reactor. This gave K_{ms} = 8 mg COD · mg X_a^{-1} d^{-1} at 20°C. This value, because it also satisfies the observed aerobic response, was adopted for both aerobic and anoxic conditions. Uncertainty of the values of K_{ms} in both aerobic or anoxic states, in fact, is not important, because the rate of utilization of easily biodegradable material is so high that invariably the reaction is complete well within the actual retention times normally provided.

Once the values of K'_{ms} and K''_{mp} at 20°C were established for a sludge age = 20 d and an anoxic volume fraction = 25%, simulations were done for different sludge ages and anoxic sludge fractions. From the simulated slopes of the nitrate profiles in the secondary phase of the pre-denitrification plug flow reactor and in the single phase of the post-denitrification reactor, the values of K_2 and K_3 were calculated. The simulated response data indicated that (1) the magnitudes of the anoxic volume fractions have virtually no effect on the simulated K values, neither in the pre- nor in the post-denitrification reactors. (2) In the range of sludge ages from 10 to 20 days the respective K values remain substantially constant (see Fig. 6a and b). The constancy of the K values over this range of sludge ages has been noted experimentally earlier in this paper.

In order to establish the temperature dependency for the constant K''_{mp} the simulations were repeated for a temperature of 14°C using pre- and post-denitrification plug flow reactors. The value of K''_{mp} was varied until close correspondence between experimental and observed nitrate profiles was obtained. As for the aerobic model, an Arrhenius type of temperature dependency was assumed, i.e.

$$K''_{mpT} = K''_{mp20}\,\theta_p^{T-20}. \tag{48}$$

It was found that at 14°C the best correspondence between the experimental and simulated K_2 and K_3 values was obtained when K''_{mpT} was given a temperature dependency of $\theta_p = 1.06$. In Fig. 6(a) and (b) the experimental and simulated values of K_2 and K_3 for a temperature of 14°C are shown plotted as a function of the sludge age. By using $\theta_p = 1.06$ it is possible therefore to obtain good correlation of the observed and theoretical K values over the range T = 14–20°C. Dold *et al.* (1980) accepted a temperature dependency of $\theta_p = 1.029$ for K'_{mp} in their analysis of aerobic systems. However, when the temperature dependency $\theta_p = 1.06$ was inserted for K'_{mp} to simulate experimental data of aerobic systems at 12°C, it was found that the predicted response was fractionally closer to the observed one than in the case where $\theta_p = 1.029$ was used. The value of $\theta_p = 1.06$ therefore seems to be acceptable for both aerobic and anoxic environments. The temperature dependency of K_{msT} for the process was determined also by fitting the simulated to the observed profile in the reactor. Similarly from the slope of the nitrate profiles in the primary phase of a pre-denitrification plug flow reactor the temperature dependency of K'_{ms} could be established when again an Arrhenius type of temperature dependency was assumed, i.e.

$$K'_{msT} = K_{ms20} \cdot \theta_s^{T-20}. \tag{49}$$

The closest correlation was obtained with $\theta_s = 1.20$.

Once the temperature dependencies of K_{mp} and K_{ms} were known, simulations were done over the temperature range between 12 and 22 C. In Fig. 7 the simulated values of K_1, K_2 and K_3 are shown plotted as a function of the temperature for sludge ages R_s = 10 d and R_s = 20 d. The experimentally observed K values are also indicated.

Having calibrated the model it is now of interest to inquire if there is a simple quantitative link between the K values and the kinetic constants for substrate utilization. This can be done as follows: The rate of nitrate utilization as expressed in equation (46) can be divided into a rate associated with the utilization of easily biodegradable material, dN_1/dt, and a rate as-

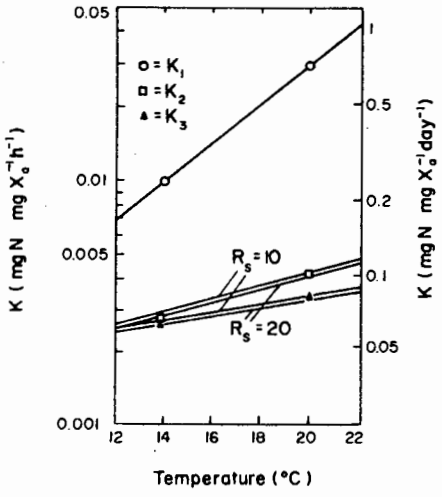


Fig. 7. Simulated and experimental denitrification rate constants K_1, K_2 and K_3 vs temperature for $R_s = 10$ and $R_s = 20$ d.

sociated with the utilization of slowly biodegradable material, dN_2/dt, where

$$dN_1/dt = -\left[(1 - PY_h)\cdot\frac{A}{2.86}\right]\cdot X_a \quad (50)$$

and

$$dN_2/dt = -\left[\left(\frac{1 - PY_h}{2.86}\right)C\right]\cdot X_a \quad (51)$$

i.e.

$$dN_n/dt = dN_1/dt + dN_2/dt. \quad (52)$$

Substituting for A from equation (18), one obtains:

$$dN_1/dt = -(1 - PY_h)K_{ms}\cdot S_{bs}\cdot X_a/((S_{bs} + K_{ss})2.86). \quad (53)$$

As the half saturation value, K_{ss}, is very small, ($K_{ss} = 5$ mg COD·l^{-1}) the expression $K_{ms}\cdot S_{bs}/(K_{ss} + S_{bs})$ remains virtually constant and equal to K_{ms} until S_{bs} falls to very low values. Consequently, the function in square brackets in equation (50) remains virtually constant and hence equation (7) applies:

$$dN_1/dt = \Delta N_1/t_p \simeq -K_1X_a \quad (54)$$

where

$$K_1 = (1 - PY_h)\cdot K_{ms}\cdot S_{bs}/(K_{ss} + S_{bs})/2.86$$

as

$$S_{bs}/(K_{ss} + S_{bs}) \simeq 1$$

hence,

$$K_1 \simeq (1 - PY_h)\cdot K_{ms}/2.86. \quad (55)$$

The mass of denitrified nitrate, from equation (46), is directly proportional to the mass of substrate utilized in the denitrification reaction, the proportionality constant being $(1 - PY_h)/2.86$. In a pre-denitrification reactor normally all the influent easily biodegradable substrate is completely utilized and hence the nitrate removal associated with the utilization of easily biodegradable material can be expressed as

$$\Delta N_{1s} = (1 - PY_h)\cdot S_{bsi}\cdot/2.86. \quad (56)$$

Substituting for $Y = 0.45$ and $P = 1.48$:

$$\Delta N_{1s} = 0.1168\, S_{bsi}. \quad (57)$$

Now in unsettled and approximately so in settled municipal waste flows

$$S_{bsi} = 0.24\, S_{bi}. \quad (58)$$

Substituting in equation (57)

$$\Delta N_{1s} = 0.028\, S_{bi} \quad (59)$$

giving the same value as that experimentally observed, in equation (16). This reaction applies only in the pre-denitrification reactor, in the post-denitrification reactor S_{bs} is essentially zero.

With regard to the slowly biodegradable COD fraction, the nitrate utilization rate can be expressed by substituting equation (20) in equation (37):

$$dN_2/dt = (1 - PY_h)K''_{mp}\cdot P\cdot X_s\cdot X_a/(PX_s + K_{sp}X_a)/2.86. \quad (60)$$

Considering the pre-denitrification reactor, X_s is large and due to the slow rate of the reaction there is only a small change in X_s between the beginning and the end of the plug flow reactor. Consequently, again it is possible to write

$$\Delta N_2/R_{1a} = K_2X_a \quad (61)$$

even though the constancy exhibited by K_2 arises from a different cause from that for K_1. Considering the post-denitrification reactor, X_s generally is very small arising principally from storage of lysis products. The concentration of X_s hardly changes from the beginning to the end of the reactor and consequently again the slope, dN_3/dt, can be expressed as in equation (60):

$$\Delta N_{3a}/R_{3a} = K_3X_a.$$

The behavioural patterns described above have been observed elsewhere. Heideman (1979) analysed the denitrification behaviour in batch experiments, using mixtures of sludge and influent municipal sewage. By observing the change of nitrate and soluble COD with time he found that (1) the nitrate time profile was very similar to that observed by Marais & Ekama (1976) in pre-denitrification plug flow reactors, i.e. there was a high denitrification rate in the primary phase followed by a lower rate in the secondary phase. (2) Cessation of the primary phase occurred when the soluble COD concentration attained a constant value, i.e. when all the easily biodegradable substrate was utilized. (3) The ratio between the nitrate removal due to the high rate, i.e. ΔN_{1s}, and the decrease in the soluble COD concentration, i.e. S_{bsi}, was

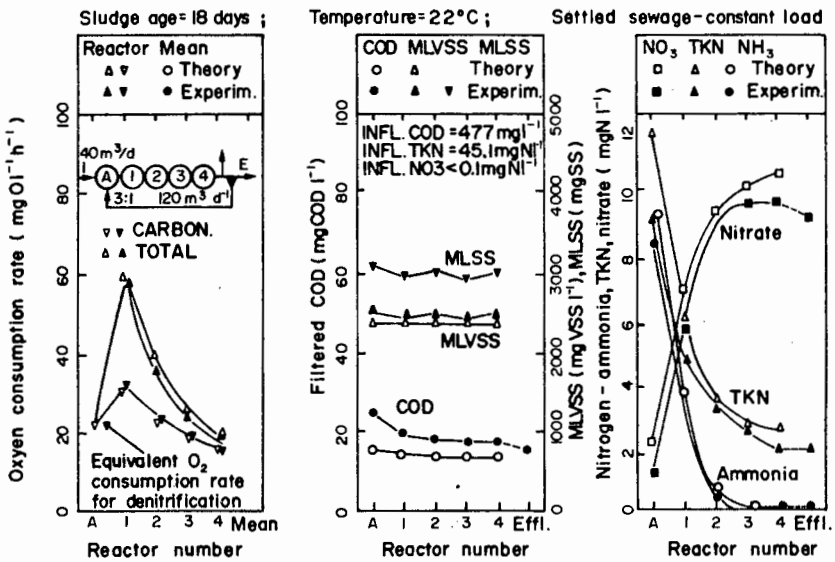


Fig. 8. Experimental and simulated response of series reactor anoxic/aerobic system under constant flow and load conditions. (Plant design parameters in Table 1.)

repeatedly found to be in the range 0.11–0.12 mg N·mg COD^{-1}, the same as determined above [equation (57)]. Furthermore, the two phase behaviour was observed only when sludge and influent sewage were mixed; batch denitrification tests with sludge only yielded linear profiles akin to the post-denitrification plug flow nitrate profiles. Unfortunately, it was not possible to calculate the active sludge concentration from the data supplied by Heideman, so that the denitrification rate constants (in terms of mg N·mg X_a^{-1}·d^{-1}) could not be determined.

From the analysis above the denitrification "constants" K_1, K_2, K_3 have no fundamental kinetic significance; they are a result of a combination of kinetic reactions which, fortuitously, show little variation with sludge age (in the range from 10 to 20 days) at any selected temperature in the range 12–22°C. Both from an experimental and a practical point of view it would appear that for design, the acceptance of constant values for K_1, K_2 and K_3 at any selected temperature is not unreasonable and hence suitable for estimating the denitrification achievable under constant flow and load conditions.

MODEL VERIFICATION

The plug flow experiments allowed calibration of the general nitrification-denitrification model. It now remains to check if the calibrated model applies to completely mixed reactors under more general conditions of flow and load.

The predictive power of the calibrated model was tested by comparing the simulated data with those observed in completely mixed series reactor nitrification-denitrification systems under a variety of flow and load conditions. In addition, tests were carried out in a single reactor system where the environment was made sequentially aerobic and anoxic.

The series reactor systems were all space dependent (Ekama & Marais, 1978) and time dependency could be superimposed by cyclicly varying the flow and/or load conditions. An experimental investigation was carried out at pilot plant level under both time independent and time dependent conditions at Daspoort Sewage Works, Pretoria. The process configuration is shown in Fig. 8. It consists of a series of 5 equal-sized reactors each of 5 m^3 capacity, the first reactor anoxic, the remainder aerobic, with an underflow recycle to the anoxic zone of 3:1. Sewage characteristics and design parameters are listed in Table 1. Two series of tests were carried out.

The first series was carried out under time independent and space dependent conditions by having a constant influent flow and load. In Fig. 8 the averages of 27 daily measurements of the process variables, i.e. oxygen uptake rate, VSS, COD, TKN, ammonia and

Table 1. Anoxic/aerobic pilot plant design parameters and sewage characteristics (see Fig. 8)

Parameters	Constant load	Cyclic load
Configuration	Series	Series
No. of reactors	5 × 5 m^3	5 × 5 m^3
Total volume (m^3)	25	25
Sludge age (d)	18	18
Influent flow (m^3·d^{-1})	40	60
Influent COD (mg l^{-1})	477	mean 363
Influent TKN (mg N·l^{-1})	45.1	mean 33.5
μ_{mn}	0.41	0.41
pH	7.8	7.8
Temperature	22°C	22°C
Underflow recycle ratio	3:1	2:1

nitrate concentrations are shown plotted. Also shown are the predictions by means of the model.

The second series was carried out under time and space dependent conditions by imposing a daily cyclic load as follows: A constant influent flow was drawn directly from the discharge of a primary settling tank of a full scale works, so that the natural diurnal variations of the COD, TKN and ammonia concentrations of the waste flow was imposed on the process.

The same process variables as in the first series were measured at regular intervals over a number of 24 h test periods. The results of one 24 h test are shown in Fig. 9(a), the simulated results in Fig. 9(b).

The simulations of Figs 8 and 9 were obtained assuming values of all the kinetic constants [equations (34–45)] to be identical to those reported by Dold *et al.* (1980), for aerobic systems and calculating K''_{mp} from equation (48). With regard to the maximum growth rate of nitrifiers, μ_{nm20}, Dold *et al.* (1980) found repeatedly that its value is dependent on the waste flow source and can vary from 0.15 to 0.65 d^{-1}. Its value must therefore be determined by fitting the simulated nitrate profiles to the experimental for every individual waste flow.

In the first series of tests, i.e. under constant flow and load conditions, (Fig. 8), there was good correspondence between simulated and the mean experimental data, for all the measured variables, in each reactor. In the second series of tests, i.e. under cyclicly varying load conditions (Fig. 9) it was not possible to obtain the same close correspondence. A problem here was that the reproduceability of experimental response between different runs was rather poor. The imposition of cyclic flow and load conditions exerts severe demands on the predictive power of the model and from a theoretical point of view this system should be the most satisfactory for checking the validity of the general model. Unfortunately, the quasi plug flow conditions in the series system tend to cause unstable response if a perturbation appears either in the value of a kinetic constant or in the flow and load conditions. Such effects can be averaged out if the cyclic test is repeated a number of times and a mean effect calculated but the magnitude of work involved makes this approach rather impractical.

At laboratory scale, Wilson & Marais (1976) tested a two reactor process under cyclic conditions (Fig. 10). The process consisted of a pre-denitrification

At laboratory scale, Wilson & Marais (1976) tested a two reactor process under cyclic conditions (Fig. 10). The process consisted of a pre-denitrification reactor (1.0 l.) and an anaerobic reactor (6.4 l.) in series with an underflow recycle ratio of 1.5:1 with respect to the mean daily influent flow. A square wave flow and load pattern (12 h constant feed, 12 h no feed) was imposed with a flow of 15 l d^{-1} of settled municipal sewage from the Athlone-Cape Town outfall (COD = 570 mg·l^{-1}; TKN = 54 mg·l^{-1}). This waste flow contained a high proportion of industrial discharge. Figure 10 shows the simulated and observed concentrations of nitrate and TKN in the anoxic and aerobic reactors and the oxygen uptake rate in the aerobic reactor for one experiment over a period of 26 h. The average values of effluent COD and volatile solids concentration are also indicated (Fig. 10c).

To obtain the best correlation between the experimental and simulated data it was necessary to assume that the fraction of easily biodegradable material was only 10% of the biodegradable influent COD concentration (instead of the average fraction of 24% reported by Ekama and Marais) and that the maximum specific substrate utilization rate constant for slow biodegradable material had to be reduced from 3.0 to 2.3 mg COD·mg $X_a^{-1}\cdot d^{-1}$, still keeping $K''_{mp} = 0.38\,K'_{mp}$ [equation (48)]. In addition a maximum specific growth rate of nitrifiers $\mu_{nm20} = 0.17\,d^{-1}$ had to be used to describe the nitrification behaviour. The lower values can be ascribed to the high proportion of industrial waste in the influent sewage. With these adaptions it was possible to simulate very closely the experimental data (see Fig. 10).

In all the test series reported experience indicated that instability, i.e. poor reproduceability in response arose either from series configurations operation, or cyclic variation load, or hydraulic effects due to precipitous changes in flow rate, or a combination of these. Consequently, in a third investigation it was sought specifically to find a system in which severe demands would be imposed on the predictive power on the model but the factors inducing instability would not be present. A system found to satisfy these requirements was a single reactor system operating under constant flow and load, but with alternate periods of aerobic and anoxic conditions. A reactor of 6 l. was operated at a sludge age of 6 days and a temperature of 20°C. Sewage was obtained from the Strandfontein outfall, Cape Town. The influent flow was kept at a constant value of 20 l d^{-1} and the influent concentrations of COD and TKN as near as possible to 500 and 45 mg·l^{-1} respectively. During an experiment the oxygen supply to the mixed liquor was interrupted for certain time periods each day and the concentrations of TKN, ammonia, nitrate, COD and VSS were observed over both the anoxic and the aerobic periods. During the aerobic periods the oxygen uptake rate was measured. A short sludge age of 6 days was selected as this assures a high rate of denitrification per unit sludge mass. By varying the lengths of the anoxic periods the possible effects of these periods on nitrification and denitrification also could be evaluated.

Figure 11 shows the experimental and simulated response for an anoxic period of 5 h, followed by an aerobic period of 19 h. The oxygen uptake rate (and equivalent oxygen uptake rate during the anoxic period, Fig. 11a), volatile solids and filtered COD concentrations (Fig. 11b), TKN, ammonia and nitrate concentrations (Fig. 11c, d and e respectively) are plotted vs time. In addition, the alkalinity time profile

(a)

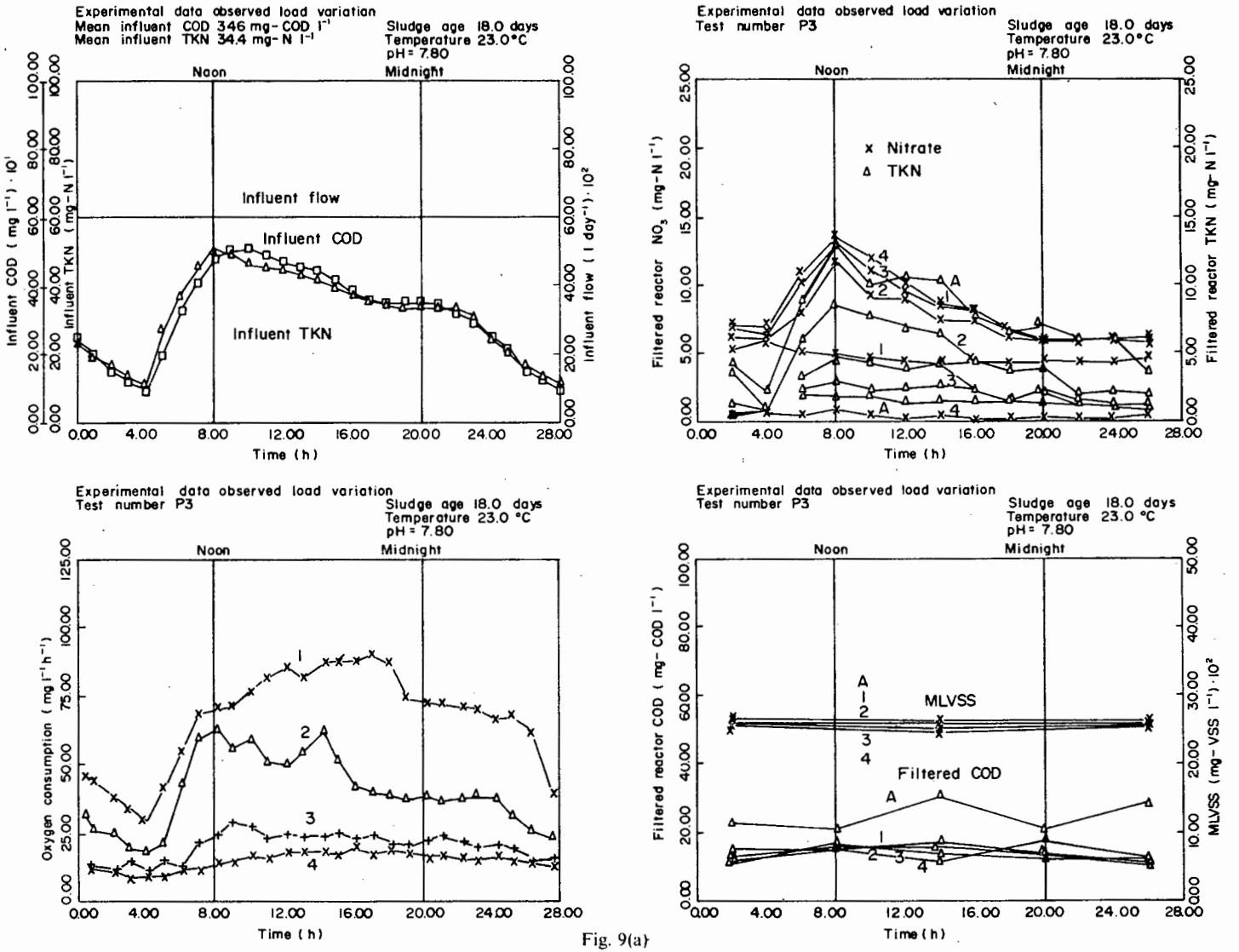

Experimental data observed load variation
Mean influent COD 346 mg-COD l⁻¹
Mean influent TKN 34.4 mg-N l⁻¹
Sludge age 18.0 days
Temperature 23.0°C
pH = 7.80
Noon
Midnight
Influent flow
Influent COD
Influent TKN
Influent COD (mg l⁻¹) · 10⁻¹
Influent TKN (mg-N l⁻¹)
Influent flow (l day⁻¹) · 10⁻²
Time (h)
Experimental data observed load variation
Test number P3
Sludge age 18.0 days
Temperature 23.0°C
pH = 7.80
Nitrate
TKN
Filtered reactor NO₃ (mg-N l⁻¹)
Filtered reactor TKN (mg-N l⁻¹)
Experimental data observed load variation
Test number P3
Sludge age 18.0 days
Temperature 23.0 °C
pH = 7.80
Oxygen consumption (mg l⁻¹ h⁻¹)
Experimental data observed load variation
Test number P3
Sludge age 18.0 days
Temperature 23.0 °C
pH = 7.80
MLVSS
Filtered COD
Filtered reactor COD (mg-COD l⁻¹)
MLVSS (mg-VSS l⁻¹) · 10⁻²

Fig. 9(a)

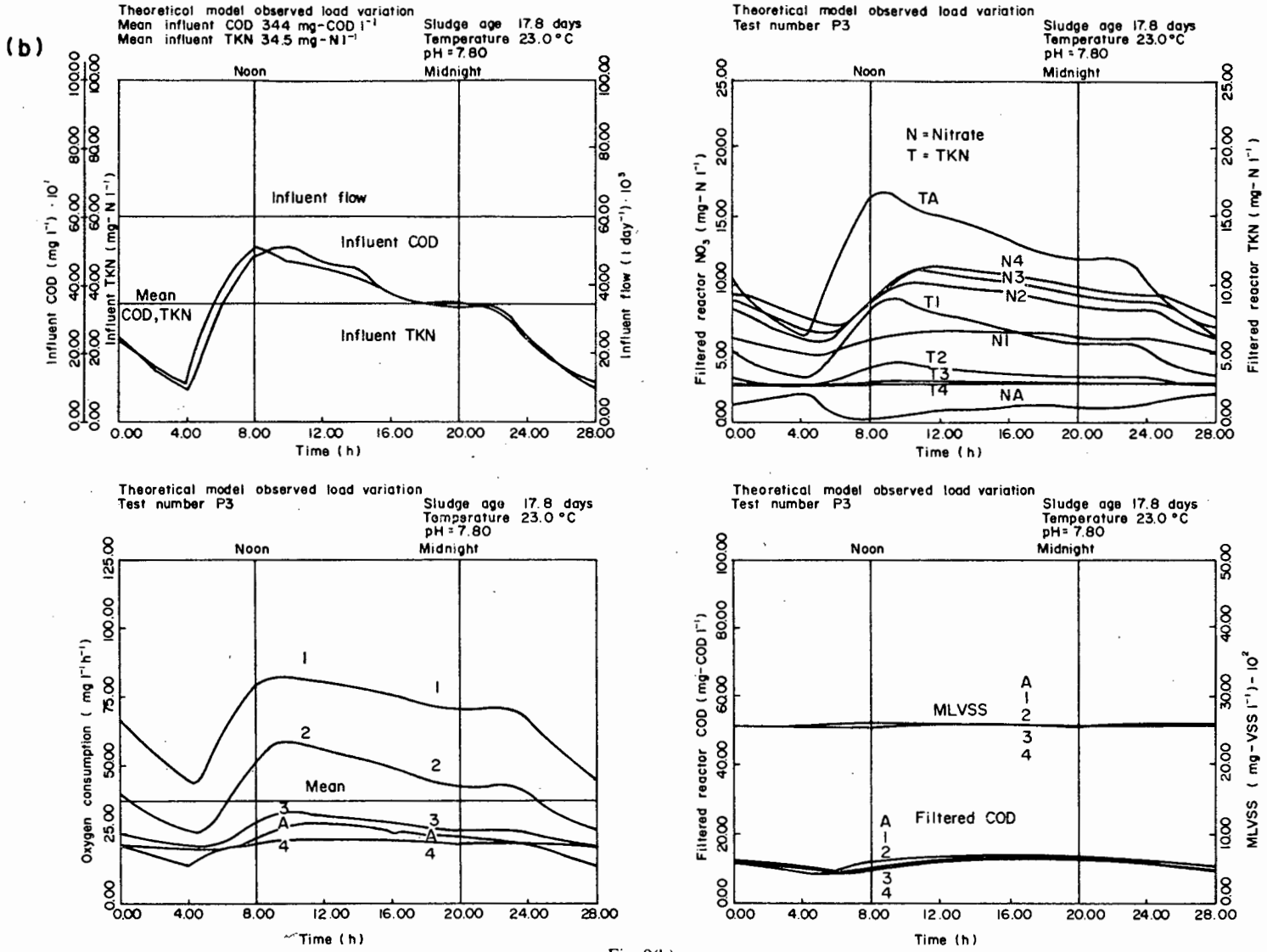
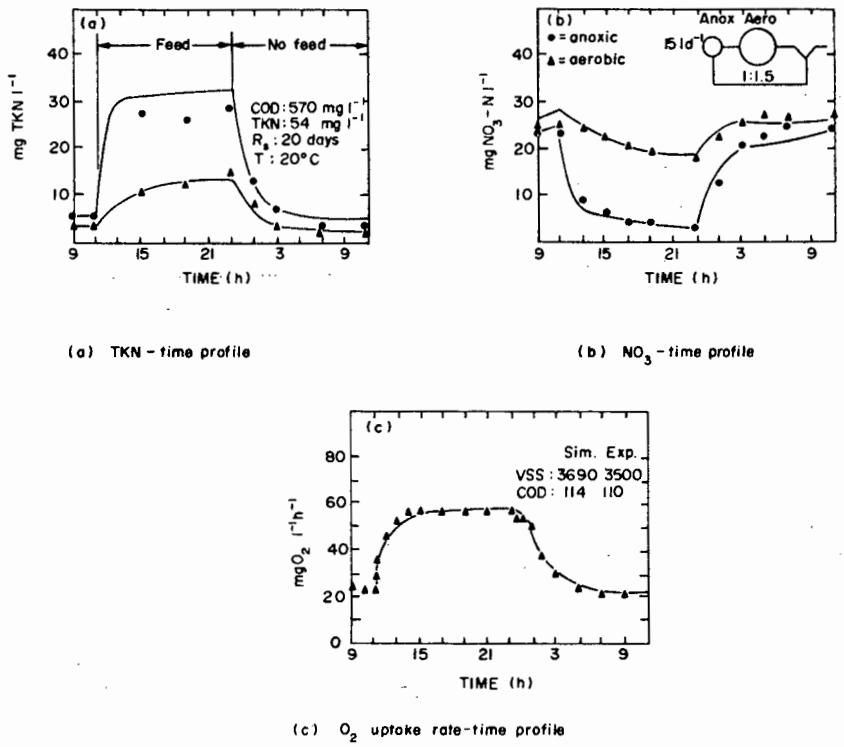


Fig. 9(b).

Fig. 9. Experimental and simulated response of an anoxic/aerobic series reactor system under cyclic load conditions (configuration shown in Fig. 8; plant design parameters in Table 1). (a) Experimental response. (b) Simulated response.



(a) TKN – time profile

(b) NO_3 – time profile

(c) O_2 uptake rate–time profile

Fig. 10. Experimental and simulated response of TKN, NO_3 and O_2 uptake rate in a Modified Ludzack Ettinger system under cyclic (square wave) flow and load conditions.

was measured and simulated (Fig. 11f) assuming stoichiometric changes due to nitrification and denitrification and taking into account the effect of ammonification (Scearce *et al.*, 1980).

The following values were obtained for the fits shown in Fig. 11: $f_{ca} = 0.0$; $K'_{mp} = 2.2$; $K''_{mp} = 0.66$; $\mu_{nm20} = 0.45$. Note that the value for K'_{mp} is lower than the mean value found by Dold *et al.* (1980) and that the value of K'_{mp} is lower than that calculated by equation (48). The fraction of easily biodegradable COD, f_{ca}, was zero instead of the mean value of 24% of the biodegradable COD. Because these constants deviated from the mean values derived by Dold *et al.* (1980) from their accumulated data, the validity of the experimental procedure with the single reactor system was checked by carrying out experiments during the same time, utilizing four modified Ludzack Ettinger systems each with different anoxic volume fractions, treating the same sewage as the single reactor system. Simulation of these systems utilizing the constants derived from the single reactor system gave excellent correspondence with the experimental data. It was therefore concluded that the very low values of K'_{mp} and K''_{mp} and f_{ca} were due to the sewage characteristics and could not be ascribed to the experimental set up using a single reactor system.

An interesting observation from the nitrification behaviour at 20°C was that the close correspondence between the experimental and simulated nitrate profile (Fig. 11e) implies that the imposed anoxic period of five hours did not appear to have any noticeable influence on the nitrification behaviour subsequently; no lag phase was apparent, and the rate of nitrification attained its maximum value immediately on reimposing aerobic conditions. This conclusion is substantiated by the good correspondence between simulated and experimental profiles of TKN, ammonia, oxygen uptake rate and alkalinity during the aerobic period.

Even though the cyclic changes of all the variables (except the VSS and filtered COD concentrations) were substantial, reproducibility in experimental response was excellent. Changes in simulated response on changing the values of the kinetic constants in the expressions for nitrification and denitrification indicated that the response is very sensitive to the values assigned to these constants. Hence, by means of the experimental method described above in conjunction with the simulated model it was possible not only to obtain reliable experimental data but also accurate estimates of the kinetic constants for a particular waste flow and constitutes a most convenient and time saving method to determine the kinetic constants for substrate utilization, nitrification and denitrification.

Taking all the experimental work into account it would appear that the model characterized by the differential equations (18)–(33) and (46) gives a good description of all the nitrification–denitrification systems with the proviso that the numerical values of

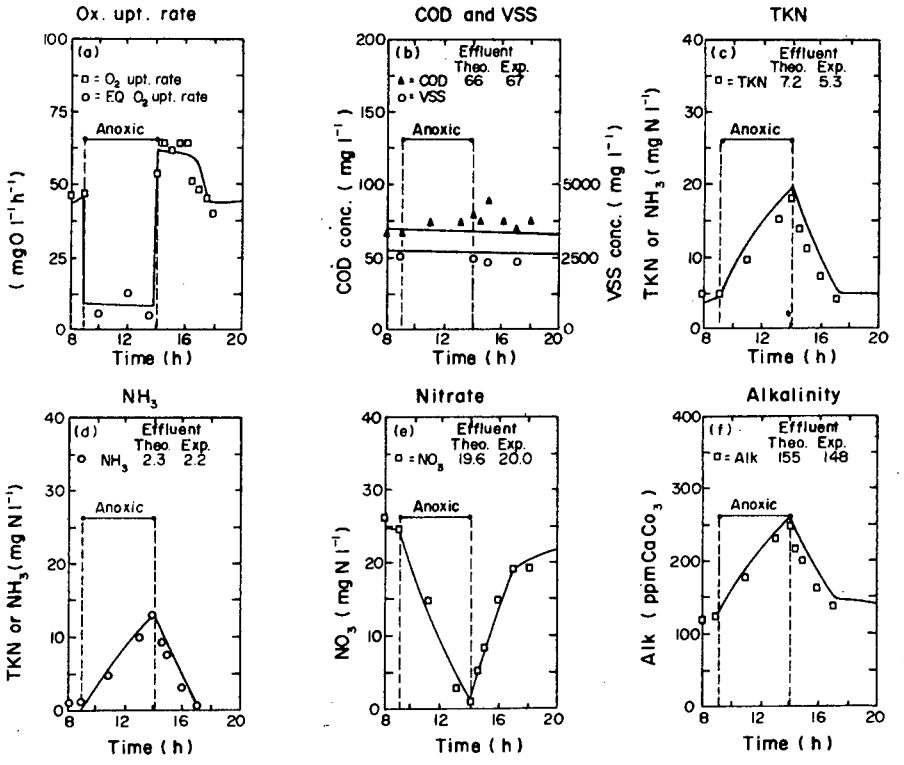


Fig. 11. (a) Oxygen uptake rate; (b) VSS and filtered COD; (c) TKN; (d) NH_3; (e) NO_3; and (f) Alkalinity as a function of time in a single reactor anoxic/aerobic system under constant flow and load conditions.

some of the kinetic constants are affected by the characteristics of the influent sewage. The constants that seem to be most sensitive to changes in influent sewage characteristics are the maximum specific growth rate of the nitrifiers (reflected in the maximum nitrification rate) and to a lesser extent the maximum specific utilization rate constant for slowly biodegradable material (reflected in the utilization rate of dissolved oxygen and the denitrification rate). Also it was found that the fraction of easily biodegradable material in sewage is subjected to considerable variations. This implies that the numerical values of the empirical denitrification rate "constants" K_1, K_2, K_3 and α also depend on the sewage characteristics and that accurate values for a particular waste flow can only be determined by experiment, most conveniently by utilizing the single reactor constant flow and load-sequential aerobic/anoxic procedure outlined above. In such an investigation it is preferable to use fresh sewage every day rather than to store a batch and to feed it over a longer period. In the latter case the possibility of an atypical response of the system due to a coincidental singularity in the characteristics of the influent is greater.

CONCLUSIONS

(i) The bi-substrate active-site death-regeneration model developed by Dold *et al.* (1980) to describe the aerobic activated sludge system, can be extended to provide a reliable description of the kinetics of the nitrification–denitrification single sludge process under both constant and daily cyclic conditions of flow and load.

(ii) The extension requires no change in the basic equations describing the aerobic process, only a change in the value of one of the constants in the expression defining the substrate utilization rate for slowly biodegradable particulate material when an anoxic environment is required. Nitrification is affected only in so far that growth of the nitrifiers takes place only in an aerobic environment but death in both aerobic and anoxic environments.

(iii) Under constant load and flow conditions the denitrification kinetics can be adequately described by the empirical equation $\Delta N_s = KX_a$. Depending on the position of the denitrification reactor in the process configuration K has different values. These K values have no fundamental kinetic significance; they are only apparent constants, the result of a combination of kinetic reactions which fortuitously show little variation under normal operational conditions.

(iv) The fundamental kinetic constants in the expressions for substrate utilization and nitrification are affected by the wastewater characteristics. The variability of the constants for nitrification is greater than that for substrate utilization.

(v) A single reactor system operated under sequential anoxic and aerobic periods constitutes a convenient experimental set up for the determination of the values of the kinetic constants of nitrification and substrate utilization and of denitrification in the anoxic phases.

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REFERENCES

Barnard J. L. (1973) Biological denitrification. *Wat. Pollut. Control* **72**, 705–720.

Barnard J. L. (1976) A review of biological phosphorus removal in the activated sludge process. *Water S.A.* **2**, 163.

Carlson D. E. (1971) Nitrogen removal and identification for water quality control. OWRR Project No. 4040, Department of Civil Engineering, University of Washington.

Chong J. P. & Morris J. E. (1962) Studies on the utilization of nitrate by micrococcus denitrificans. *J. gen. Microbiol.* **29**, 301.

Christensen M. H. & Harremoes P. (1977) Biological denitrification of sewage: A literature review. *Prog. Wat. Technol.* **8**, 509–555.

Christensen M. H. & Harremoes P. (1977) Biological denitrification in water treatment. Report 72-2. Department of Sanitary Engineering, Technical University of Denmark.

Dold P. L., Ekama G. A. & Marais G. v. R. (1980) A general model for the activated sludge process. *Prog. Wat. Technol.* **12**, 47–77.

Ekama G. A. & Marais G. v. R. (1978) The dynamic behaviour of the activated sludge process. Research Report No. 27, Department of Civil Engineering, University of Cape Town.

Ekama G. A., van Haandel A. C. & Marais G. v. R. (1979) The present status of research on nitrogen removal: A model for the modified activated sludge process. Presented at the *Symposium on Nutrient Removal*, C.S.I.R., Pretoria. To be published by the Water Research Commission of South Africa.

Heide B. A. (1975) Aerobe en verdergaande zuivering van afval water in zeer Laagbelaste actief-slib systemem, deel II, Rapport A 77, Inst. voor milieuhygiëne en gesondheidstechniek TNO, Delft. (in Dutch).

Heideman J. A. (1979) Sequential nitrification–denitrification in a plug flow activated sludge system U.S. Environmental Protection Agency, Cincinnati, OH, Report EPA 600/2-79-157.

Lawrence A. W. & McCarty P. L. (1970) Unified basis for biological treatment design and operation. *J. sanit. Engng Div., Proc. Am. Soc. civ. Engrs* **96**, 757–778.

Ludzack F. J. & Ettinger M. B. (1962) Controlling operation to minimize activated sludge effluent nitrogen. *J. Wat. Pollut. Control Fed.* **34**, 920–931.

Marais G. v. R. & Ekama G. A. (1976) The activated sludge process: Steady state behaviour *Water S.A.* **2**, 163–200.

Marsden M. G. & Marais G. v. R. (1976) The rôle of the primary anoxic reactor in denitrification and biological phosphorus removal. Research Report No. 19, Department of Civil Engineering, University of Cape Town.

McCarty P. L. (1964) Thermodynamics of biological synthesis and growth. In *Second International Conference on Water Pollution Research*, pp. 169–199. Pergamon Press, New York.

McLaren A. R. & Wood R. J. (1976) Effective phosphorus removal from sewage by biological means. *Water S.A.* **2**, 47–50.

Scearce S. N., Benninger B. W., Weber A. S. & Sherrard Y. H. (1980) Predictions of alkalinity changes in the activated sludge process. *J. Wat. Pollut. Control Fed.* **52**, 399–405.

Stensel H. D., Loehr R. C. & Lawrence A. W. (1973) Biological kinetics of suspended growth denitrification. *J. Wat. Pollut. Control Fed.* **45**, 249–261.

Stern L. B. & Marais G. v. R. (1974) Sewage as electron donor in biological denitrification. Research Report No. 7, Department of Civil Engineering, University of Cape Town.

Wilson D. E. & Marais G. v. R. (1976) Adsorption phase in biological denitrification. Research Report No. 11, Department of Civil Engineering, University of Cape Town.

Wuhrmann K. (1964) Nitrogen removal in sewage treatment processes. *Vehr. Int. Ver. Theor. Angew. Limnol.* **15**, in German

Wat. Sci. Tech. Vol.14, Capetown, pp.443-461, 1982 0273-1223/82/000443-19$09.50/0

OPTIMIZATION OF NITROGEN REMOVAL IN THE SINGLE SLUDGE ACTIVATED SLUDGE PROCESS

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Abstract

Optimal design of nitrification-denitrification (N-D) systems reduces to obtaining maximum denitrification subject to the constraint of efficient nitrification. Under constant flow and load conditions simple approximate highly accurate formulae are developed to describe the N-D system. Selection of the N-D configuration is found to be crucially influenced by the TKN/COD (influent) ratio, μ_{nm}, maximum and minimum temperature and sludge age. In terms of these factors design charts are presented which rapidly allow the best configuration and sizes of the anoxic and aerobic reactors to be selected.

INTRODUCTION

In 1981, van Haandel, Ekama and Marais extended the general aerobic nitrification model of the activated sludge process, developed by Dold, Ekama and Marais (1980), to include denitrification in the single sludge process. The model was shown to give a very good account of the experimental response observed over a wide range of reactor configurations (single and series reactor systems including unaerated reactors), influent flow and load conditions (constant and daily cyclic flow and load), and process parameters (sludge age 2 to 25 days; temperature 12 to 22°C; recycle ratios 1 to 7), and, alternating aerobic and unaerated phases in a single reactor system. For design purposes a difficulty with the model is that it requires the system configuration, load conditions and process parameters to be defined, whereupon the process response can be simulated - it does not give information on the design of the system for optimum nitrogen removal, except by repeated trial selection of configuration and some process parameters. In this paper an "optimization" procedure will be presented which allows rational selection of the process configuration and operational parameters to achieve maximum removal of nitrogen in a single sludge N-D system, within the constraints set on the system.

BASIC CONSIDERATIONS

A framework for optimal design cannot be established by considering the problem in its generality - simplified conditions of flow and load, in this case constant flow and load, must be assumed. The response of the design thus obtained, under the expected daily cyclic flow and load conditions, then, always can be checked by simulation using the general model and, by trial, adjustments attempted to achieve improved removals. However, from experience, optimal designs based on constant flow and load usually seem to be so near the optimum for cyclic conditions that there is little, if anything, to be gained in attempting to improve on the "optimal"

solution, particularly when taking into account the uncertainties always present in (1) the expected flow and load patterns; (2) the expected values of some of the kinetic constants, particularly that for nitrification; and (3) some of the sewage characteristics, particularly the fraction of readily biodegradable COD. The simplest approach in developing the optimization procedure is first to formulate the denitrification and nitrification behaviour separately, and thereafter, to integrate the two effects subject to the following provisos: (1) a high efficiency of nitrification must be assured at all times, and (2) removal of nitrate generated in the system must be complete or at a maximum.

DENITRIFICATION MODEL

The model for denitrification, on which the optimization procedure will be based, is an approximation derived from the observed and simulated behaviour of N-D processes under *constant flow and load conditions* (van Haandel *et al*, 1981): In a single sludge N-D process consisting of a series of reactors with a plug flow anoxic* reactor preceding a completely mixed aerobic reactor (pre-denitrification or pre-D reactor) and another plug flow reactor subsequent to the aerobic reactor (post-denitrification or post-D reactor) (see Fig. 1), the denitrification behaviour can be accurately described by a set of linear expressions derived as follows: From observation, verified by simulation using the general model (see Fig. 2), the denitrification behaviour in the pre-D reactor can be described by two virtually linear nitrate-time relationships. The first is due to the rapid utilization of the readily biodegradable COD in the influent, S_{bsi}; the second to the less rapid utilization of slowly biodegradable particulate COD derived both from the influent and from death and lysis of the active organism mass. In the post-D reactor only one linear relationship is present, also due to the utilization of slowly biodegradable particulate COD principally from death and lysis.

The rates in each of the three phases can be expressed, to very good approximation, by the relationship $dN/dt = KX_a$. The rate constants, K, remain virtually unchanged in the range of sludge ages from 10 to 25 days, are independent of nitrate concentration, dependent only on temperature. Van Haandel *et al* (1981) showed that the K "constants" are not basic kinetic ones; rather, they are the result of complex interactions of the various kinetic reactions that govern the process, and it is only fortuitous that the K values remain relatively constant in the range of sludge ages given above. Two further observations of great utility are:

(1) The phase in the pre-D reactor, due to S_{bsi}, terminates after a few minutes, (when this COD fraction has been utilized); the *extent* of denitrification achieved is directly proportional to the mass of readily biodegradable COD utilized. Usually the time this reaction persists is of little interest as the retention time in the plug flow reactor normally exceeds the time for this phase to be completed.

(2) Sludge production in an anoxic-aerobic system is not distinguishably different from that in a completely aerobic system and the fractions, active, endogenous and inert can be calculated by the formulations of Marais and Ekama (1976) [see Appendix]. The active mass concentration, X_a, in the system is formulated as:

$$X_a = S_{bi}Y_hR_s/[(1+b_{hT}R_s)R_h] = S_{bi}C_r/R_h \quad (1)$$

where $$C_r = Y_hR_s/(1+b_{hT}R_s) \quad (2)$$

The equations for denitrification in the pre- and post-denitrification reactors can now be set out in greater detail:

Pre-denitrification reactor: In this reactor denitrification is characterized by two linear reactions: a rapid reaction that persists only for a time R'_{a1}, and a slow reaction that persists for the total time in the reactor, R_{a1}. The removal is given by the difference between the reactor influent and effluent nitrate

*Anoxic is defined as an environment in which oxygen is absent but nitrate is present.

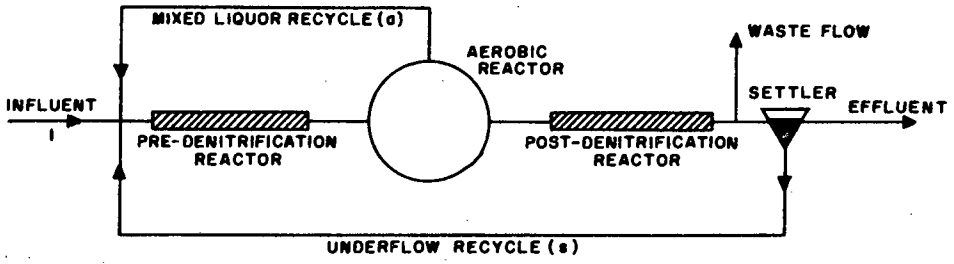


Fig. 1. Configuration including pre- and post-denitrification plug flow reactors.

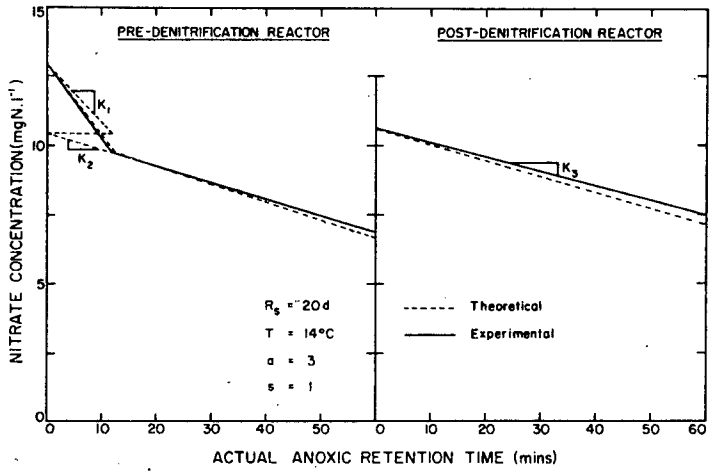


Fig. 2. Comparison of experimentally observed and theoretically predicted nitrate concentration-retention time profiles in the pre- and post-denitrification reactors.

concentrations, ΔN_{al}, i.e.

$$\Delta N_{al} = K_1 X_a R'_{al} + K_2 X_a R_{al} \quad (3)$$

Taking account of the recycles to the pre-denitrification reactor, as shown in Fig. 1, the flow rate through the reactor is Q(1+a+s), where Q is the average influent flow rate to the plant, i.e. the flow passes (1+a+s) times through the reactor and the *system* removal, ΔN_{ls}, is given by

$$\Delta N_{ls} = K_1 X_a R'_{al} (1+a+s) + K_2 X_a R_{al} (1+a+s) \quad (4)$$

The *nominal* retention time, R, is defined by V(reactor)/Q and is related to *actual* retention time, R_a, as follows:

$$R = R_a(1+a+s) \quad (5)$$

and Eq.(4) reduces to

$$\Delta N_{ls} = K_1 X_a R'_1 + K_2 X_a R_1 \quad (6)$$

Usually $R'_1 < R_1$, in which event the first reaction is complete; its extent of denitrification is proportional to S_{bsi}, i.e. $\alpha' S_{bsi}$. For convenience, van Haandel *et al* (1981) formulated $\alpha' S_{bsi}$ in terms of the total biodegradable COD in the influent, S_{bi}, as follows: $S_{bsi} = f_{bs} S_{bi}$, hence $\alpha' S_{bsi} = \alpha' f_{bs} S_{bi} = \alpha S_{bi}$; Eq.(6) reduces to

$$\Delta N_{ls} = \alpha S_{bi} + K_2 X_a R_1 \quad (7)$$

Substituting for X_a from Eq. (1), noting that R_1/R_h equals the anoxic sludge mass fraction, f_{x1}:

$$\Delta N_{1s} = (\alpha + K_2 C_r f_{x1}) S_{bi} \quad (8)$$

where f_{x1} = (mass of sludge in pre-D reactor)/(mass of sludge in system).

Post-denitrification reactor: In this reactor denitrification is characterised by a single linear rate. The system removal, ΔN_{3s}, is given by

$$\Delta N_{3s} = K_3 X_a R_3 = K_3 C_r f_{x3} S_{bi} \quad (9)$$

where f_{x3} = (mass of sludge in post-D reactor)/(mass of sludge in system).

System reduction for a process having both pre- and post-denitrification reactors is found by adding Eqs. (8 and 9):

$$\Delta N_s = \alpha S_{bi} + K_2 X_a R_1 + K_3 X_a R_3 \quad (10)$$

Three notes of importance are:

(1) The equations above are valid only if nitrate is present throughout the plug flow reactor, in the same fashion that the equation for the rate of oxygen utilization in the aerobic process is valid only if oxygen is present.

(2) The equations are valid also for completely mixed anoxic reactors; experiments and simulations using the general model, with similar sized plug flow or completely mixed anoxic reactors, under constant flow and load conditions, give virtually identical nitrate reductions.

(3) In practice the small mass flow of dissolved oxygen introduced to an anoxic reactor via the a- and s- recycles will cause a slight reduction in ΔN_s because oxygen is utilized preferentially by the organism mass. However, the effect is marginal, if the oxygen level is < 2mg/ℓ and $(a + s) \leq 5$; weighed against the uncertainties inherent in the input and other data plus the added complexity it brings into the analysis, inclusion of dissolved oxygen in the analysis has little merit.

Van Haandel *et al* (1981) showed that the magnitudes of the constants K_1, K_2, K_3 and α are dependent on the sewage characteristics and preferably should be determined experimentally. However, the K-constants differ little from one municipal waste flow to another and for all intents and purposes can be accepted as constant. The α value shows greater differences; in municipal waste flows α appears to be dependent, in part, on the industrial component but the causes for differences observed are not explicitly apparent. Average values of the constants, together with the temperature dependencies of the rate constants, for municipal waste flows as found by Marais and co-workers, are listed in Table 1.

Denitrification Potential: The denitrification potential of an anoxic reactor, D_p, is defined as the system nitrate removal that takes place in that reactor *provided nitrate is always present*. For a pre-denitrification reactor:

TABLE 1 Denitrification Constants (T = temperature in deg C)

Constant	Value	Units
K_1	$0{,}03\ (1{,}20)^{T-20}$ (T 14°C)	mg N.mg $X_a^{-1}.h^{-1}$
K_2	$0{,}0042(1{,}08)^{T-20}$ (T>14°C)	mg N.mg $X_a^{-1}.h^{-1}$
	$0{,}0032(1{,}03)^{T-20}$ (T<14°C)	
K_3	$0{,}0032(1{,}03)^{T-20}$ (10°C<T<25°C)	mg N.mg $X_a^{-1}.h^{-1}$
α	0,028	mg N.mg COD^{-1}

$$D_{p1} = \Delta N_{1s} = \alpha S_{bi} + K_2 X_a R_1 = (\alpha + K_2 C_r f_{x1}) S_{bi} \quad (11)$$

For a post-denitrification reactor:

$$D_{p3} = \Delta N_{3s} = K_3 X_a R_3 = K_3 C_r f_{x3} S_{bi} \quad (12)$$

For a series system including both pre- and post-denitrification reactors:

$$D_p = D_{p1} + D_{p3} = (\alpha + K_2 C_r f_{x1} + K_3 C_r f_{x3}) S_{bi} \quad (13)$$

The concept of a denitrification potential constitutes a powerful tool in developing procedures to obtain optimal nitrification-denitrification systems.

NITRIFICATION UNDER ANOXIC-AEROBIC CONDITIONS

Anoxic and Aerobic Sludge Mass Fractions

The general theory for nitrification in anoxic-aerobic systems developed by Van Haandel *et al* (1981) is founded on three assumptions:

(1) Nitrifiers grow only under aerobic conditions. The rate limiting step in their growth can be expressed in terms of Monod's equations.

(2) Death of nitrifiers occurs under both anoxic and aerobic conditions, at the same rate.

(3) The nitrification rate constants are not affected by the presence of anoxic zones in the system.

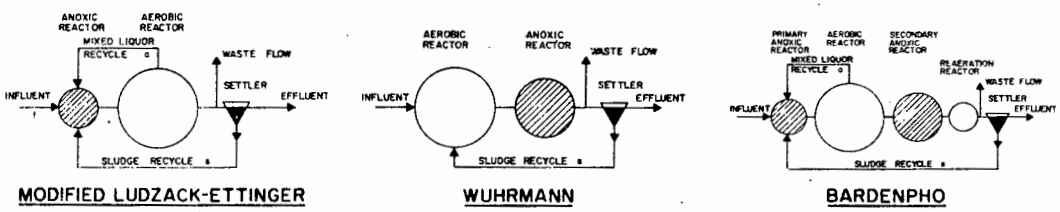
Under constant flow and load conditions, the nitrification behaviour in series reactor systems can be described accurately by simple approximate expressions if two assumptions are made:

(1) There is a uniform concentration of nitrifiers throughout the reactor system. Although death of nitrifiers occurs in all zones, growth occurs only in aerobic zones, resulting in small differences in the organism concentration from reactor to reactor. From simulations using the general model, these differences are so small that they may be neglected.

(2) The effluent ammonia concentration is equal to the ammonia concentration in the aerobic reactor. This is true only in pre-D systems where the aerobic reactor is the last in a series. In systems with a post-D reactor such as the Wuhrmann or Bardenpho configurations (Fig. 3) there is a net increase in the ammonia concentration in the post-D reactor because ammonification of TKN from lysed material exceeds de-ammonification through re-synthesis of heterotrophs. However, both simulations and experimental results (Arkley and Marais, 1981) indicate that this increase is negligibly small.

An expression for the effluent ammonia concentration, N_a, from a series reactor system with pre- and/or post-D is derived from a mass balance on the nitrifying sludge mass, MX_n. Under steady state conditions the mass of nitrifiers is constant, i.e.

$$(dMX_n/dt) = 0 = (dMX_n/dt)_g + (dMX_n/dt)_d + (dMX_n/dt)_w \quad (14)$$



MODIFIED LUDZACK-ETTINGER WUHRMANN BARDENPHO

Fig. 3. Process configurations for biological denitrification.

(1) Growth: Occurs only in the aerobic reactor and can be expressed in terms of the Monod equation

$$(dMX_n/dt)_g = V(1-f_x)\,(dX_n/dt)_g = V(1-f_x)X_n\,\mu_{nmT}.N_a/(N_a+K_{nT}) \quad (15)$$

(2) Death: Takes place in both aerobic and anoxic zones

$$(dMX_n/dt)_d = V(dX_n/dt)_d = -Vb_{nT}\,X_n \quad (16)$$

(3) Sludge Wastage: With hydraulic control of sludge age, the waste flow, q, from a reactor is defined by $q = V/R_s$, where V is the total volume of the system

$$(dMX_n/dt)_w = -qX_n = -VX_n/R_s \quad (17)$$

Substituting, and solving for effluent ammonia concentration, N_a:

$$N_a = K_{nT}(b_{nT} + 1/R_s)/[(1-f_x)\mu_{nmT} - (b_{nT} + 1/R_s)] \quad (18)$$

For completely aerobic systems ($f_x = 0$), Eq. (18) reduces to an expression very similar to that of Downing, Painter and Knowles (1964) for a single completely mixed aerobic reactor, i.e.

$$N_a = K_{nT}(b_{nT} + 1/R_s)/[\mu_{nmT} - (b_{nT} + 1/R_s)] \quad (19)$$

Comparing Eqs. (18 and 19), the inclusion of unaerated reactors is equivalent to reducing the true maximum specific growth rate of nitrifiers, μ_{nmT}, by a factor f_x (the anoxic mass fraction) to give an apparent rate, μ'_{nmT}

$$\mu'_{nmT} = \mu_{nmT}(1-f_x) \quad (20)$$

Equations (18 and 19) presuppose that nitrification does take place. The minimum sludge age, R_{sm}, for the commencement of nitrification in a single aerobic reactor is found when N_a equals the ammonia concentration available for nitrification in the influent, N_{ai}; then from Eq. (19), with $K_{nT} << N_{ai}$,

$$R_{sm} = 1/(\mu_{nmT}-b_{nT}) \quad (21)$$

Correspondingly, in anoxic-aerobic systems

$$R'_{sm} = 1/[(1-f_x)\mu_{nmT} - b_{nT}] \quad (22)$$

From Eq. (22) R'_{sm} is dependent on both, the kinetic constants μ_{nmT} and b_{nT}, *and* the aerobic sludge mass fraction, $(1-f_x)$. Conversely for a specified $R_s > R'_{sm}$ there is a minimum aerobic sludge mass fraction, $(1-f_m)$, below which no nitrification will take place. From Eq. (22), solving for $(1-f_x)$,

$$(1-f_m) = (b_{nT} + 1/R_s)/\mu_{nmT} \quad (23)$$

The aerobic sludge mass fraction must be larger than $(1-f_m)$ because a primary objective in anoxic aerobic systems is to guarantee efficient nitrification, i.e. to ensure a low effluent ammonia concentration, N_a. In evaluating the required increase in $(1-f_m)$ one approach is to specify a desired maximum effluent ammonia concentration, N_{ad}, for a fixed $R_s > R'_{sm}$, and then to calculate the minimum allowable aerobic sludge mass fraction, $(1-f_M)$; from Eq.(18), substituting N_{ad} for N_a and $(1-f_M)$ for $(1-f_x)$

$$(1-f_M) = (1 + K_{nT}/N_{ad})(b_{nT} + 1/R_s)/\mu_{nmT} = (1 + K_{nT}/N_{ad})(1-f_m). \quad (24)$$

From Eq. (24) the minimum aerobic sludge mass fraction, $(1-f_M)$, required for nitrification to a desired effluent ammonia concentration, N_{ad}, is greater by a factor $(1 + K_{nT}/N_{ad})$ than the aerobic sludge mass fraction, $(1-f_m)$, below which no nitrification can take place. The factor $(1 + K_{nT}/N_{ad})$ serves the function of a "safety factor". This approach has the disadvantage that the selection of a

desired effluent ammonia concentration, N_{ad}, is a subjective one, and small changes in N_{ad} lead to large changes in the safety factor by which $(1-f_m)$ must be increased [at 14°C, where K_{nT} = 0,5 mg N.ℓ^{-1}, a change in N_{ad} from 1 to 2 mg N.ℓ^{-1} results in a 20 per cent change in $(1-f_M)$]. A more rational approach, which is very simple to apply in design, is to specify the S_f which will ensure stable and efficient nitrification; from numerous simulations, provided $(1-f_x) \geq 1{,}25\ (1-f_m)$, nitrification will be stable and at high efficiency under both constant and cyclic flow and load conditions. Accepting a safety factor, S_f, of say 1,25, the minimum *aerobic* sludge mass fraction, $(1-f_M)$, required for efficient *and* stable nitrification is

$$(1-f_M) = S_f(1-f_m) = S_f(b_{nT} + 1/R_s)/\mu_{nmT} \qquad (25)$$

The maximum *anoxic* sludge mass fraction allowing efficient nitrification, f_M, is found by solving for f_M in Eq. (25),

$$f_M = 1 - S_f(b_{nT} + 1/R_s)/\mu_{nmT} \qquad (25a)$$

The approach set out above, of using a safety factor, has the disadvantage that the effluent quality is no longer limited to a specific value and will vary slightly, depending on μ_{nmT}. However an S_f of not less than 1,25 usually will ensure an N_a < 2 mg N.ℓ^{-1} under constant flow and load conditions, except at very low temperatures of less than about 12°C. Equation (25a) imposes no upper limit on the maximum anoxic sludge mass fraction, f_M. However,experimental observations (Arkley and Marais, 1981) indicate that settling properties of the sludge deteriorate sharply when the anoxic sludge mass fraction increases above 0,50. For this reason, a constraint on the upper limit for f_M, (f_{Max}), of 0,50 is accepted for design.

Figure 4 illustrates the effect on f_M of sludge age, μ_{nm} and T. (Temperature dependency equations for nitrification are listed in Table 2). In plotting Fig. 4 values of μ_{nm20} of 0,65 and 0,33 d^{-1}, and temperatures of 20°C and 14°C, have been selected as the approximate ranges encountered in South Africa, with S_f = 1,25.

From Fig. 4 f_M is very sensitive to the value of μ_{nm}: for a specified R_s and T, as μ_{nm} increases the *aerated* sludge mass fraction, $(1-f_M)$, required for efficient nitrification decreases. The value selected for μ_{nm} therefore is of great importance. The value of μ_{nm} appears to be specific to each waste flow; reliable evaluation of μ_{nm} can be found by experiment only. For municipal waste flows a rough guide appears to be that μ_{nm} decreases as the industrial component increases; different municipal waste flows giving $0{,}21d^{-1} \leq \mu_{nm20} \leq 0{,}65d^{-1}$ have been encountered. This wide range of expected values makes that unless a verv

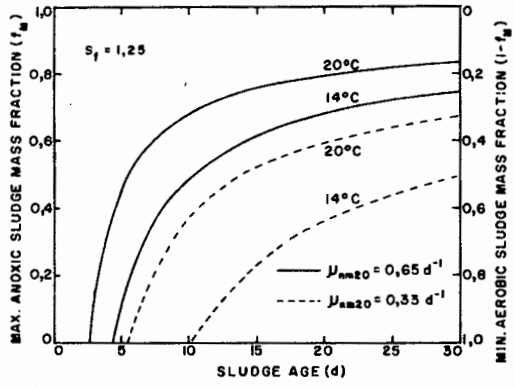


Fig. 4. Maximum allowable anoxic sludge mass fraction, f_M, or minimum aerobic sludge mass fraction required to sustain efficient nitrification versus sludge age for different μ_{nm} at 20°C and 14°C.

TABLE 2 Temperature Dependency Equations for Nitrification

$$\mu_{nmT} = \mu_{nm20}\ (1{,}123)^{T-20}$$
$$b_{nT} = 0{,}04\ (1{,}029)^{T-20}$$
$$K_{nT} = 1{,}0\ (1{,}123)^{T-20}$$

conservative design is acceptable (μ_{nm20} = 0,2 to 0,3d^{-1}), it is necessary to experimentally determine μ_{nm} for a particular flow.

The design procedure for nitrification in anoxic-aerobic systems requires, *inter alia*, calculation of the maximum allowable anoxic sludge mass fraction (f_M) based on: (1) a selected safety factor, S_f; (2) the system R_S; (3) the minimum T in the plant, T_{min}, and (4) μ_{nm} at that temperature. If the procedure to determine f_M is followed for the lowest T, then efficient nitrification at any $T > T_{min}$ always will be guaranteed.

Nitrification capacity: Marais and Ekama (1976) showed that only a fraction of the influent TKN, N_{ti}, is available for nitrification: a concentration is incorporated in the sludge mass, N_S, and there is a residual organic nitrogen concentration in the effluent, N_O, i.e. the ammonia concentration available for nitrification is

$$N_p = N_{ti} - N_S - N_O \tag{26}$$

Expressions for N_S and N_O have been developed by Marais and Ekama (1976):

$$N_S = f_n[Y_h(1+fb_{hT}X_aR_s)(1-f_{us}-Pf_{up})/(1+b_{hT}R_s)+f_{up}]S_{ti} \tag{27}$$

$$N_O = [N_{oi}+f_n(1-f)b_{hT}X_a/(1-PY_h)]/(1+K_{rT}X_aR_h) \tag{28}$$

The *nitrification capacity* is defined as the concentration of influent TKN in an anoxic-aerobic system that is converted to nitrate. Taking into account the effluent ammonia concentration, N_a, but disregarding the concentration of nitrite, the nitrification capacity is given by the difference between the ammonia concentration available for nitrification (N_p) and N_a.

$$N_c = N_p - N_a = N_{ti} - N_S - N_O - N_a \tag{29}$$

From Eqs. (18 and 29) it is clear that N_C is dependent, *inter alia*, on the anoxic sludge mass fraction. It has been noted that efficient nitrification is a necessary requirement in design of anoxic-aerobic systems. In addition, an objective is to remove all the nitrate by denitrification, or, where this is not possible, to remove the maximum amount without impairing the efficiency of nitrification. Therefore, in the analysis of nitrification and denitrification, it is necessary to evaluate N_C subject to the condition that, at any sludge age, denitrification is at its allowable maximum, i.e. the anoxic sludge mass fraction is f_M. For a specified sludge age $R_S > R'_{Sm}$, f_M is determined from Eq. (25a): the corresponding nitrification capacity, $(N_C)_{f_M}$ is determined from Eqs. (18,27,28 and 29). In Fig. 5 $(N_C)_{f_M}$ is plotted as a function of R_S for a series of influent TKN/COD ratios with S_{ti} = 500 mg COD.ℓ^{-1} at 14°C and S_f = 1,25 (i.e. $N_{ad} \simeq 2$ mg N.ℓ^{-1}). The maximum anoxic sludge mass fraction (f_M) for the assumed value of $\mu_{nm14} = 0{,}18d^{-1}$ is also shown in the Figure. [The following sewage characteristics were accepted: f_{us} = 0,10 mg COD. mg COD^{-1}; f_{up} = 0,09 mg VSS.mg COD^{-1}]. In the Figure the effluent organic nitrogen concentration, N_O, is estimated at 1,0 mg N.ℓ^{-1}.

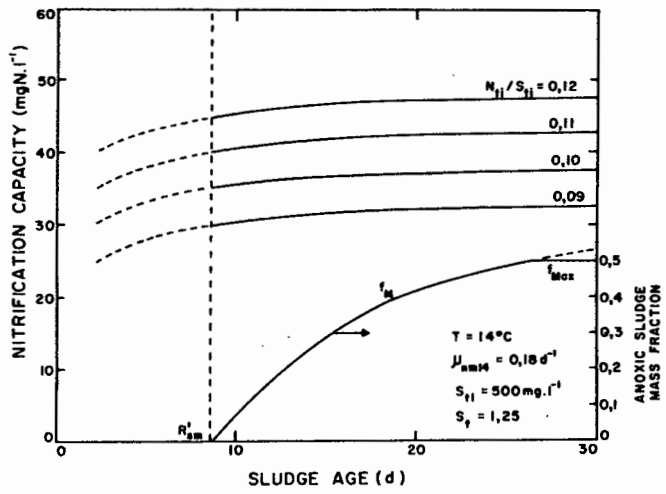


Fig. 5. Nitrification capacity, N_C, as a function of sludge age for different influent TKN/COD ratios. The corresponding maximum anoxic sludge mass fraction is also plotted.

APPLICATION IN DESIGN

The objective in optimization of N-D single sludge systems is to minimize the total soluble effluent nitrogen concentration, subject to the constraints of (1) efficient nitrification, and (2) $f_{Max} \leq 0{,}50$. In design additional constraints usually will be imposed on operational parameters: for example, the sludge age and the recycle ratios cannot be increased at will; long sludge ages result in large plant volumes per unit COD treated and high recycle ratios may introduce sufficient oxygen in the anoxic zones to nullify denitrification.

The concentration of nitrate generated in the aerobic zone of a process is directly related to the influent TKN, N_{ti}, whereas the nitrate removal in the anoxic zone of a process is, amongst others, proportional to the influent COD concentration, S_{ti}. Consequently, the influent TKN/COD ratio forms a measure of the mass of nitrate that can be removed by denitrification. These characteristics establish the importance of the parameter N_{ti}/S_{ti} in the design of optimal nitrification-denitrification systems.

Basis for Design

To satisfy the prerequisite for efficient nitrification f_M must be determined for a selected R_S and μ_{nm} from Eq. (25a), using an S_f of, say 1,25. As the system must operate over a range of T the critical T for the determination of f_M is always the *minimum* expected, for, at the lowest temperature, μ_{nm} will attain its lowest value and hence f_M will attain the lowest limiting value still ensuring efficient nitrification. Once f_M has been determined this anoxic sludge mass fraction must be subdivided into pre- and post-D fractions, f_{x1} and f_{x3} respectively, with $f_{x1} + f_{x3} = f_M$. The division is made by means of Eqs. (31 and 33) (developed later); what is important is that the division is based on the *maximum* expected T for the reason that, as T decreases K_2 and K_3 approach each other in value, until at 14°C and below the two values coincide - at 14°C and below the division into pre- and post-D sludge mass fractions, in fact, becomes immaterial, i.e. any division can be made provided that $f_{x1} > f_{min}$. At T_{max}, however, the division must be specific to T_{max} to attain the maximum removal of nitrate at T_{max}. At intermediate T, for the selected division, (1) the removal will decrease from the maximum at T_{max} to the minimum at T_{min}, and (2) the removal will be maximized because K_2 exceeds K_3.

Subdivision of f_M into f_{x1} and f_{x3} is governed by the following:

(1) To utilize fully the denitrification potential, D_p, of a reactor, the nitrate introduced to the reactor must be equal to D_p.

(2) Per unit volume the D_p of a pre-denitrification reactor always exceeds that of the post-denitrification reactor.

(3) Except under infinitely large recycles, to obtain complete nitrate removal it is necessary that the system includes both pre- and post-D reactors.

(4) The recycle ratios cannot be increased at will; there is an upper limit, set by the cost of providing the recycles, or, by the mass of oxygen introduced to anoxic reactors via the recycles.

(5) To maintain reasonable mixed liquor settling properties f_M must not exceed 0,50 even if Eq. (25a) indicates a larger fraction.

To explain the behaviour of the system we will approach it in reverse to the problem that must be solved in practice. Instead of, as is usual, specifying the influent TKN/COD ratio and determining the required sludge age and anoxic sludge mass fraction, f_x, we will assume a specified R_s and a specified f_x (with the proviso that $f_x < f_M$) and then determine the maximum TKN/COD ratio which the system can completely denitrify. We will also assume that the total recycle (a+s) can be made as high as required. Once f_x is fixed the D_p for the system will depend on the subdivision of f_x into f_{x1} and f_{x3} [Eq. (13)]. For any selected subdivision there is a limit to the influent TKN/COD ratio that this division can completely denitrify, given by Eq. (34) (to be developed). If the influent TKN/COD ratio to be treated is higher that this TKN/COD limit then the nitrate present in the effluent can be reduced by increasing f_{x1} and decreasing f_{x3} (keeping $f_{x1}+f_{x3}=f_x$) and calculating a new set of recycles, or, expressed in a different way: the allowable TKN/COD ratio for complete denitrification can be increased always by increasing f_{x1} at the expense of f_{x3}, *provided the recycles can have any value required*, until, when $f_{x1}=f_x$ (i.e. a Modified Ludzack-Ettinger (MLE) system), the upper limit to the TKN/COD that can be completely denitrified is attained. In this case (a+s) will be found to be infinite. If yet higher influent TKN/COD ratios must be treated, this is possible only by increasing f_x until f_x equals f_M, when the absolute limiting TKN/COD ratio that can be completely denitrified is attained. Hence, providing that (a+s) can be increased *ad infinitum*, the maximum TKN/COD ratio the system can denitrify completely is when $f_{x1} = f_x = f_M$.

If an upper limit is set to (a+s) then the same procedure as described above can be followed with the proviso that the solution terminates when (a+s) attains the limiting ratio. Taking the situation where $f_x = f_M$, it will be found that the maximum influent TKN/COD ratio that can be accommodated to give zero nitrate in the effluent will be less than that if (a+s) can increase to infinity: also, f_{x3} will now not equal zero, and f_{x1} and f_{x3} will both have positive values. If f_{x1} is now increased at the expense of f_{x3}, keeping (a+s) = maximum, then a higher influent TKN/COD ratio is required to load the pre-D reactor to its D_p, and although the system nitrate removal is increased, nitrate will be present in the effluent. When $f_{x1} = f_x = f_M$ (i.e. an MLE configuration) the TKN/COD ratio for maximum nitrate removal will be attained but the nitrate in the effluent also will have increased. For yet higher TKN/COD ratios the effluent nitrate concentration will increase by an amount equal to the additional TKN because the pre-D reactor is loaded to higher than its D_p and no additional nitrate is removed.

To express the above in a quantitative manner it is preferable to develop the theory for the Bardenpho and MLE configurations separately.

Bardenpho Configuration - Complete Nitrate Removal

The Bardenpho configuration includes both pre- and post-D reactors (Fig. 3); when designed such that the effluent nitrate concentration is zero; denitrification is said to be complete. With a- and s-recycles, a fraction, a/(a+s+1), of the concentration of nitrate present in the aerobic reactor is recycled to the pre-D reactor and the remaining fraction, (s+1)/(a+s+1), is discharged to the post-D reactor. For complete denitrification the amount of nitrate available for denitrification in each of the anoxic reactors (N_{av1} and N_{av3}) must equal the D_p of these reactors, respectively:

(1) In the pre-denitrification reactor:

$D_{p1} = N_{av1}$, and

$$(\alpha + K_2 C_r f_{x1}) S_{bi} = N_c \, a/(a+s+1) \tag{30}$$

$$\text{i.e.} \quad f_{x1} = [(N_c/S_{bi})a/(a+s+1)-\alpha]/(K_2 C_r) \tag{31}$$

(2) In the post-denitrification reactor:

$D_{p3} = N_{av3}$, and

$$K_3 C_r f_{x3} S_{bi} = N_c \, (s+1)/(a+s+1) \tag{32}$$

$$\text{i.e.} \quad f_{x3} = [(N_c/S_{bi})(s+1)/(a+s+1)]/(K_3 C_r) \tag{33}$$

The maximum ratio of N_c/S_{bi} for which complete denitrification is possible, $(N_c/S_{bi})_o$, is found by combining Eqs. (31 and 33), noting that $f_{x1} + f_{x3} = f_M$:

$$(N_c/S_{bi})_o = \frac{\alpha + K_2 C_r f_M}{a/(a+s+1) + (K_2/K_3)(s+1)/(a+s+1)} \tag{34}*$$

In Eq. (34), C_r and f_M are both functions of R_S [see Eqs. (2 and 25a)]; consequently the basic parameter against which $(N_c/S_{bi})_o$ should be evaluated is R_S, taking due cognizance of the effect of the recycle ratios, 'a' and 's'. Equation (34) cannot be applied without restriction: in Eq. (34) it is implicitly assumed that S_{bsi} is utilized completely in the pre-D reactor; this imposes a constraint on (1) the minimum allowable pre-D sludge mass fraction, f_{x1}, and (2) the minimum allowable a-recycle. Also, in design, constraints will be imposed on (3) f_M i.e. $f_M \leq f_{Max}$, and (4) the maximum allowable a- and s-recycle ratios. Consequences of these constraints are:

(1) Minimum allowable f_{x1}: The pre-D sludge mass fraction, f_{x1}, must be sufficiently large to ensure complete utilization of S_{bsi} in the pre-D reactor. From Eqs. (6 and 7) the minimum pre-D sludge mass fraction, f_{min}, required for complete utilization of S_{bsi} is:

$$f_{min} = \alpha/(K_1 C_r) \tag{35}$$

Van Haandel and Marais (1981) determined the minimum sludge age, R_B, for which Eq. (34) is valid, i.e. the sludge age above which f_{x1} is greater than f_{min} in the Bardenpho process with complete denitrification:

$$R_B = \frac{1 + A \, S_f/\mu_{nmT}}{A(1-S_f b_{nT}/\mu_{nmT}) - b_{hT}} \tag{36}$$

where $A = a \, Y_h K_1/[\alpha(s+1)(1+(K_1+K_2)/K_3)]$

(2) Minimum allowable a-recycle: A further requirement for complete utilization of S_{bsi} imposes a constraint on the minimum allowable a-recycle ratio: a minimum

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*It is convenient to relate the ratio (N_c/S_{bi}) to the influent TKN/COD ratio, (N_{ti}/S_{ti}). From Eq. (29)

$$N_c/S_{bi} = (N_{ti}-N_s-N_o-N_a)/[(1-f_{us}-Pf_{up})S_{ti}]$$

$$= N_{ti}/[S_{ti}(1-f_{us}-Pf_{up})] - (N_s+N_o+N_a)/[S_{ti}(1-f_{us}-Pf_{up})]$$

In a particular design the value of $(N_s+N_o+N_a)/[S_{ti}(1-f_{us}-Pf_{up})]$, will be known: for raw sewage the value is approximately 0,03 mg N.mg COD^{-1}, which gives the approximation: $(N_{ti}/S_{ti}) = (N_c/S_{bi})(1-f_{us}-Pf_{up}) + 0{,}03$ (37)

a-recycle, a_{min}, is required such that the mass of nitrate available in the pre-D reactor, N_{avl}, is sufficient to remove S_{bsi}, i.e.

$$N_c a_{min}/(a_{min}+s+1) = \alpha S_{bi}(K_1+K_2)/K_1 \quad (38)$$

$$\text{or } a_{min} = \alpha(s+1)/[(N_c/S_{bi})_o K_1/(K_1+K_2) - \alpha] \quad (39)$$

Equation (39) is an implicit relationship in a_{min}: a_{min}, for a specified R_s and T, can be found by trial using Eqs. (34 and 39). For the range of R_s 15 to 30 days, as T increases from 14°C to 20°C, a_{min} decreases from approximately 2 to 1. Consequently, providing the a-recycle ratio is at least 2, this consideration will not come into effect.

(3) Maximum allowable f_M, i.e. f_{Max}: $(N_c/S_{bi})_o$ increases with increasing R_s because C_r and the associated f_M both increase with R_s [Eqs. (2 and 25a), respectively]. Whereas the change in C_r is relatively small for R_s > 10 days, the change in f_M is more marked (see Fig. 4). However, the increase in f_M is limited to f_{Max}, due to the need to preserve good settling characteristics, i.e. $f_M \leq f_{Max} = 0{,}50$ (as discussed earlier). The sludge age, R_{so}, at which f_M attains the limiting value, f_{Max}, is found from Eq. (25a), with $f_M = f_{Max}$:

$$R_{so} = S_f/[\mu_{nmT}(1-f_{Max})-S_f b_{nT}] \quad (40)$$

For $R_s > R_{so}$, $f_M = f_{Max}$ and the increase in $(N_c/S_{bi})_o$ with increasing R_s is due only to the increase in C_r which is virtually inconsequential; see Fig. 6.

(4) Maximum allowable recycles: For a specified R_s the ratio for which complete denitrification is possible, $(N_c/S_{bi})_o$, increases with increasing s- and a-recycle ratios. Hence, to accommodate a high influent (N_c/S_{bi}) ratio (a+s) should be as large as possible. Usually the underflow recycle ratio (s) will be fixed by the requirements for effective functioning of the secondary settler; normally s ≃ 1. With regard to the a-recycle, theoretically it can have any value up to infinity, but as it increases the concomitant increase in $(N_c/S_{bi})_o$ declines rapidly for a > 4; this feature is discussed later*.

The effects of sludge age and the magnitude of the a-recycle on the N_c/S_{bi} ratio for which complete denitrification is possible, and on f_{x1}, is illustrated in the design chart shown in Fig. 6: $(N_c/S_{bi})_o$ is plotted as a function of R_s for different a-recycle ratios (a = 2,4,6,8) and a fixed s-recycle ratio of 1. Figure 6 is developed by following a simple step by step procedure:

Step 1 : Specify the expected minimum and maximum sewage temperatures (T_{min} = 14°C and T_{max} = 20°C here); the underflow recycle ratio (s=1, here), and μ_{nm} at the minimum temperature.
Step 2 : Determine R_{so} (where $f_M = f_{Max} = 0{,}50$) from Eq. (40) for T_{min} using a safety factor, S_f, of 1,25 ($\mu_{nm14} = 0{,}18\ d^{-1}$, here).
Step 3 : Select an a-recycle.
Step 4 : Determine R_B from Eq. (36) for T_{min}.
Step 5 : For values of R_s in the range R_B to R_{so}; repeat Steps 6 to 8.
Step 6 : Determine f_M from Eq. (25a) for T_{min} using S_f = 1,25.
Step 7 : Determine $(N_c/S_{bi})_o$ from Eq. (34) for T_{min} and T_{max} using *only* the value of f_M from Step 6. [C_r is given by Eq. (2)].
Step 8 : Determine f_{x1} from Eq. (31) for T_{max} using $(N_c/S_{bi})_o$ for T_{max} from Step 7. [C_r is given by Eq. (2)].
For values of R_s greater than R_{so} repeat Steps 6 to 8 with the exception that $f_M = f_{Max}$.

*From Eq. (34) it is apparent that at 14°C, when K_2 equals K_3, $(N_c/S_{bi})_o$ is not dependent on the a-recycle providing that a > a_{min14}; *the maximum a-recycle should therefore be selected for the maximum temperature.*

From Fig. 6 it is apparent that there is little merit in increasing the a-recycle above 4 to 6 as the increase in $(N_c/S_{bi})_o$ is then marginal; in fact, an increase may reduce the denitrification capacity of the pre-denitrification reactor through excessive introduction of dissolved oxygen.

Bardenpho Configuration - Incomplete Nitrate Removal

For a specified sludge age, R_s, and a maximum allowable a-recycle ratio, if the value of (N_c/S_{bi}) for the influent exceeds $(N_c/S_{bi})_o$ then complete denitrification is not possible and nitrate appears in both the effluent and the underflow recycle. In the pre-D reactor the nitrate available for denitrification, N_{av1}, is

$$N_{av1} = N_c\, a/(a+1) + s\, N_{ne} \tag{41}$$

The extent of denitrification per unit volume is greater in the pre-D reactor than in the post-D reactor; in order to use this, the denitrification potential of the pre-D reactor, D_{p1}, should be increased by increasing f_{x1} at the expense of f_{x3}, until D_{p1} equals the nitrate available, N_{av1}, at the maximum recycle ratios, i.e. from Eqs. (11 and 41),

$$D_{p1} = (\alpha + K_2 C_r f_{x1}) S_{bi} = N_c\, a/(a+s+1) + s\, N_{ne} \tag{42}$$

From a mass balance around the post-D reactor, the effluent nitrate concentration is given by

$$N_{ne} = N_c/(a+s+1) - D_{p3}/(s+1) \tag{43}$$

Substituting for D_{p3} from Eq. (12), noting that $f_{x3} = f_M - f_{x1}$, Eq. (43) becomes

$$N_{ne} = N_c/(a+s+1) - K_3 C_r (f_M - f_{x1}) S_{bi}/(s+1) \tag{43a}$$

Substituting Eq. (43a) for N_{ne} in Eq. (42) and solving for f_{x1} gives the pre-D sludge mass fraction for optimal nitrate removal:

$$f_{x1} = \frac{[(a+s)/(a+s+1)](N_c/S_{bi}) - \alpha - [s/(s+1)]\, K_3 C_r f_M}{C_r\,(K_2 - [s/(s+1)]\, K_3)} \tag{44}$$

Knowing f_{x1} the nitrate effluent quality can be calculated from Eq. (43a). As the value of (N_c/S_{bi}) increases, the value of f_{x1} increases correspondingly until, in the limit, $f_{x1} = f_M$, i.e. all of the anoxic sludge mass fraction is located in the pre-D reactor, and the optimal process configuration becomes that for the MLE process (Fig. 3). This limiting (N_c/S_{bi}) ratio, $(N_c/S_{bi})_1$, is found by setting f_{x1} equal to f_M in Eq. (44), i.e.

$$(N_c/S_{bi})_1 = (\alpha + K_2 C_r f_M)(a+s+1)/(a+s) \tag{45}$$

Modified Ludzack-Ettinger (MLE) Configuration

The ratio $(N_c/S_{bi})_1$ defining the transition between the Bardenpho and the MLE process as the process for optimal denitrification is determined by Eq. (45). As was the case with $(N_c/S_{bi})_o$, Eq. (45) cannot be applied without restriction: to ensure complete utilization of S_{bsi} in the anoxic reactor constraints must be imposed on (1) the minimum allowable anoxic sludge mass fraction, f_M, and (2) the minimum total recycle ratio, (a+s).

(1) Minimum allowable f_M: For complete utilization of S_{bsi} in the anoxic reactor the f_M must, at least, equal the minimum pre-D sludge mass fraction, f_{min}. The minimum sludge age, R_{MLE}, for which f_M equals f_{min} can be found by equating Eqs. (25a and 35) for f_M and f_{min},

$$R_{MLE} = (\alpha\, \mu_{nmT} + S_f K_1 Y_h)/[K_1 Y_h (\mu_{nmT} - S_f b_{nT}) - \alpha\, b_{hT} \mu_{nmT}] \tag{46}$$

(2) Minimum allowable total recycle, (a+s): A minimum total recycle, (a+s), is

required such that the mass of nitrate available in the pre-D reactor, N_{av1}, is sufficient to remove S_{bsi}, i.e.

$$N_c(a+s)/(a+s+1) = S_{bi}(K_1+K_2)/K_1 \quad (47)$$

$$\text{or } (a+s)_{min} = \frac{\alpha\,(K_1+K_2)/K_1}{(N_c/S_{bi})_1\,K_1/(K_1+K_2)-\alpha} \quad (48)$$

For a specified R_s and T, $(a+s)_{min}$ can be found by trial using Eqs. (45 and 48): for the range of R_s and T usually encountered $(a+s)_{min}$ is very small, approximately 0,5: consequently this constraint is of little importance in design.

The effects of sludge age and the magnitude of the a-recycle on $(N_c/S_{bi})_1$ is best assessed in a design chart similar to the one for $(N_c/S_{bi})_o$: in Fig. 7 $(N_c/S_{bi})_1$ is plotted as a function of R_s for different a-recycle ratios (a = 2,4,6,8) and a fixed s-recycle ratio of 1. A simple step by step procedure again can be followed in developing Fig. 7.

Steps 1 and 2 : as before.
Step 3 : Select an a-recycle.
Step 4 : Determine R_{MLE} from Eq. (46) for T_{min}.
Step 5 : For values of R_s in the range R_{MLE} to R_{so}, repeat Steps 6 and 7.
Step 6 : As before.
Step 7 : Determing $(N_b/S_{bi})_1$ from Eq. (45) for T_{min} and T_{max} using *only* the value of f_M from Step 6. [C_r is given by Eq. (2)].
For values of R_s greater than R_{so} repeat Steps 6 and 7 with the exception that $f_M = f_{Max}$.

From Fig. 7 at any R_s, as the a-recycle ratio is increased the value of $(N_c/S_{bi})_1$ decreases, i.e. the influent (N_c/S_{bi}) ratio for which the MLE process gives optimal nitrate removal decreases. Again, as for the Bardenpho process, it is evident that there is little advantage in utilizing an a-recycle of greater than 4.

If, at a selected R_s the (N_c/S_{bi}) ratio for a waste flow exceeds $(N_c/S_{bi})_1$ then it is no longer possible to remove all the nitrate available to the MLE anoxic reactor, N_{av1}, at the maximum recycle ratios; in fact the recycles can be reduced until the pre-D reactor is loaded to its denitrification potential, D_{p1}. N_{av1} is given by

$$N_{av1} = N_c(a+s)/(a+s+1) \quad (49)$$

Equating Eqs. (11 and 49), the minimum a-recycle required to load the anoxic reactor to its denitrification potential, is found by solving for 'a':

$$a = \frac{(s+1)(\alpha+K_2C_rf_M) - s(N_c/S_{bi})}{(N_c/S_{bi}) - (\alpha+K_2C_rf_M)} \quad (50)$$

There is however no absolute necessity for reducing the a-recycle ratio. Providing it is equal to or greater than the value found from Eq. (50) the effluent nitrate quality will not be affected because the nitrate removal will remain constant and equal to D_{p1}. In fact, on occasion it may be necessary to utilize a higher a-recycle to ensure that the actual anoxic retention time is short enough to maintain reasonable sludge settling characteristics; actual retention times should not greatly exceed one hour to maintain reasonable sludge settling characteristics.

Selection of Optimal Process Configuration

At any specified R_s and maximum allowable recycle ratios there are three ranges of influent TKN/COD ratios, (N_{ti}/S_{ti}), defining an optimal process configuration:

(1) Low (N_{ti}/S_{ti}) ratio, such that $(N_c/S_{bi}) \leq (N_c/S_{bi})_o$:
Complete denitrification in a Bardenpho configuration is possible. The a- and s-recycle ratios are the maximum selected. As the influent (N_c/S_{bi}) decreases

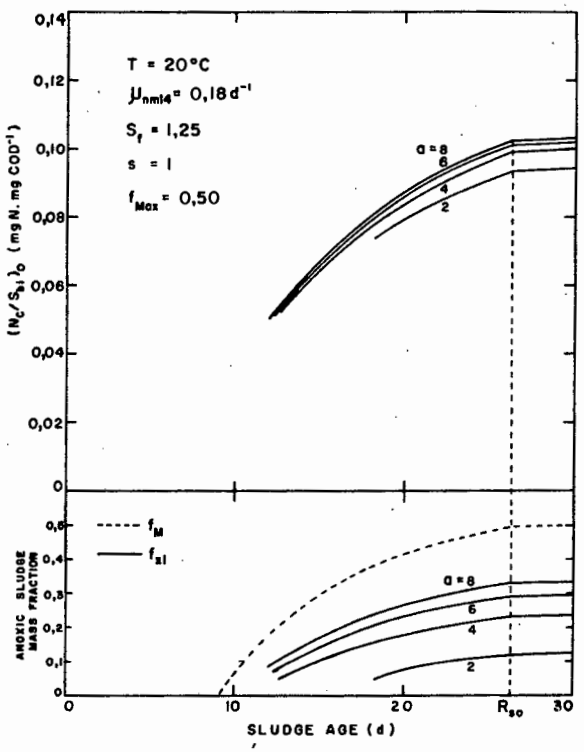

Fig. 6. N_C/S_{bi} ratio for complete denitrification, $(N_C/S_{bi})_o$, and pre-anoxic sludge mass fraction, f_{xl}, versus sludge age for different mixed liquor (a) recycle ratios.

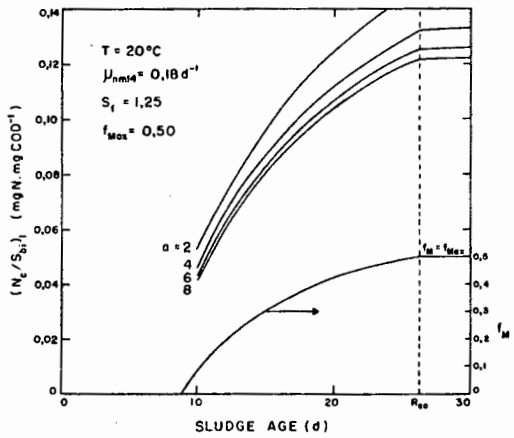

Fig.7. N_C/S_{bi} ratio for transition from Bardenpho to MLE configuration, $(N_C/S_{bi})_l$, as optimal configuration versus sludge age for different mixed liquor (a) recycle ratios.

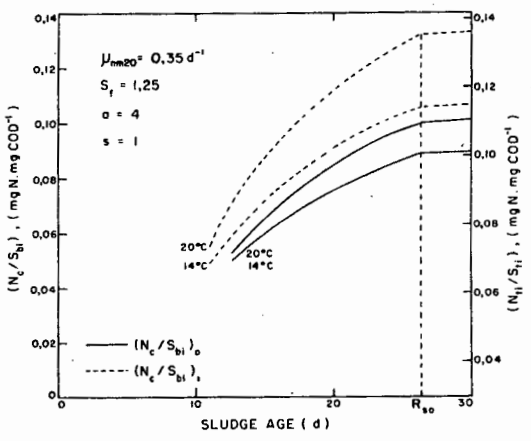

Fig.8. Design chart with $(N_C/S_{bi})_o$ and $(N_C/S_{bi})_l$ as a function of sludge age at 20°C and 14°C. Corresponding N_{ti}/S_{ti} ratios are shown on the right hand axis.

below $(N_c/S_{bi})_o$, the required f_x decreases below f_M and f_{x1} becomes disproportionately smaller with respect to f_{x3}.

(2) Medium (N_{ti}/S_{ti}) ratio, such that $(N_c/S_{bi})_o < (N_c/S_{bi}) < (N_c/S_{bi})_1$:
The optimal nitrogen removal system is the Bardenpho configuration (again with maximum recycle ratios); however, denitrification is incomplete in the post-D reactor and nitrate appears in the effluent. As (N_c/S_{bi}) increases above $(N_c/S_{bi})_o$, $f_x = f_M$, f_{x1} increases disproportionately with respect to f_{x3} until $f_{x1} = f_M$ and $f_{x3} = 0$, and the effluent nitrate concentration increases.

(3) High (N_{ti}/S_{ti}) ratio, such that $(N_c/S_{bi}) > (N_c/S_{bi})_1$:
Denitrification is incomplete: maximum nitrate removal takes place in a system without a post-D reactor, i.e. an MLE configuration ($f_x = f_{x1} = f_M$). The total maximum allowable recycle ratio, (a+s), overloads the anoxic reactor with nitrate, and (a+s) may be decreased until complete denitrification in the pre-D reactor just occurs.

In a particular design situation, the choice of process configuration is facilitated by a diagram showing the variation of $(N_c/S_{bi})_o$ and $(N_c/S_{bi})_1$ with R_s for the selected a- and s-recycle ratios. The effects of temperature can be assessed by plotting both $(N_c/S_{bi})_o$ and $(N_c/S_{bi})_1$ for the maximum and minimum anticipated mean sewage temperatures. In Fig. 8 plots for $(N_c/S_{bi})_o$ and $(N_c/S_{bi})_1$ are shown for a T_{min} = 14°C and T_{max} = 20°C, and for recycle ratios a=4 and s=1; a conservative estimate of μ_{nm} is used ($\mu_{nm14} = 0{,}18\ d^{-1}$). Figure 8 also shows, on the right hand axis, the values of (N_{ti}/S_{ti}) obtained from the approximate relationship [Eq. (37)]. (The step by step procedures for drawing up the design chart are given earlier).

CLOSURE

The analysis above identified the importance in the design of N-D single sludge processes of (1) the reference maximum specific growth rate of nitrifiers, μ_{nm20}, (2) the influent TKN/COD ratio, (3) the minimum and maximum sewage temperatures, and (4) the easily biodegradable sewage fraction (to obtain α). All these input parameters have a vital effect, in some aspect, on the design and should be determined or measured in order to obtain an optimal design. T_{min} and T_{max} can be readily assessed from full-scale plants in the region and TKN/COD ratios by direct measurement; determination of α and μ_{nm20} will present the greatest difficulty as these can be determined only by process experiment. The procedures to obtain α and μ_{nm20} as simply and as rapidly as possible will be presented in a future paper. For design with municipal effluents in the absence of any information on α, μ_{nm20} and the TKN/COD ratio, conservative design (in the sense that nitrification will be ensured with as high a nitrate removal as possible) demands a low μ_{nm20}, not greater than 0,35 d^{-1} and a high TKN/COD ratio, not less than 0,10; the value of α can be accepted at the value given here i.e. 0,028 mg N.mg COD^{-1}. If the actual μ_{nm20} is larger and the TKN/COD ratio lower than the estimates the design will be non-optimal but at least the process will function. It would seem, also, that where there is uncertainty about the expected influent TKN/COD ratio the selected process configuration should be the two reactor Modified Ludzack-Ettinger system.

ACKNOWLEDGEMENT

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APPENDIX

The biodegradable portion of the influent COD to a process is

$$S_{bi} = (1 - f_{us} - P.f_{up})\ S_{ti}$$

where

f_{us} ≈ 0,06 and 0,09 mg COD.mg COD^{-1} for raw and settled sewage, respectively.

f_{up} ≃ 0,09 and 0,02 mg VSS.mg COD^{-1} for raw and settled sewage, respectively.
Note: if garbage grinding and disposal to the sewer is practised f_{up} ≃ 0,17.

The effluent biodegradable COD concentration, S_b, is very small relative to S_{bi} (S_b < 10 mg COD.ℓ^{-1}): the mass of biodegradable COD utilized in the process per day is

$$M\Delta S_b = Q\ (S_{bi} - S_b) \simeq Q\ S_{bi}$$

The mass of active organisms in the process is

$$MX_a = [Y_h R_s/(1+b_{hT}R_s)](M\Delta S_b) \text{ where } b_{hT} = 0{,}24(1{,}029)^{T-20}$$

The endogenous organism mass in the process is

$$MX_e = f\ b_{hT} R_s\ (MX_a)$$

The mass of inert material in the process is

$$MX_i = f_{up}\ Q\ S_{ti}\ R_s$$

The total organism mass ($MX_v = MX_a + MX_e + MX_i$) is "diluted" into a volume V_p for a selected total volatile solids concentration, X_v.

$$V_p = MX_v/X_v$$

Hence the active organism concentration, X_a, is

$$X_a = MX_a/V_p = [Y_h R_s/(1+b_{hT}R_s)]\ Q\ S\ /V_p$$

$$= Y_h\ R_s\ S_{bi}/[(1+b_{hT}R_s)R_h]$$

where R_h = hydraulic retention time (V_p/Q)

LIST OF SYMBOLS

- a = mixed liquor recycle ratio
- b^* = general parameter for endogenous respiration rate, d^{-1}. Subscripts h or n refer to heterotrophic or nitrifying organisms, respectively
- C_r = sludge mass factor, mg VSS.d.mg COD^{-1}
- D_p† = denitrification potential, mg N.ℓ^{-1}
- f = unbiodegradable fraction of the active mass, 0,2 mg VSS.mg VSS^{-1}
- f_{bs} = ratio readily biodegradable (S_{bsi}): total biodegradable (S_{bi}) COD concentration in influent, mg COD.mg COD^{-1}
- f_m = maximum anoxic sludge mass fraction above which no nitrification occurs
- f_M = maximum allowable total anoxic sludge mass fraction for efficient nitrification
- f_{Max} = upper limit for anoxic sludge mass fraction
- f_n = nitrogen fraction of sludge, 0,10 mg N.mg VSS^{-1}
- f_{up} = particulate unbiodegradable fraction of the influent COD, mg VSS. mg COD^{-1}
- f_{us} = soluble unbiodegradable fraction of the influent COD, mg COD.mg COD^{-1}
- f_x† = anoxic sludge mass fraction
- K = denitrification rate constant, mg NO_3-N.mg $VSS^{-1}.h^{-1}$
- K_1 = denitrification rate constant in primary phase, mg NO_3-N.mg $X_a^{-1}.h^{-1}$

K_2 = denitrification rate constant in secondary phase, mg NO_3-N.mg $X_a^{-1}.h^{-1}$

K_3 = denitrification rate constant in post-denitrification reactor, mg NO_3-N.mg $X_a^{-1}.h^{-1}$

K_n^* = Monod half saturation coefficient for nitrification, mg NH_3-N.ℓ^{-1}

K_r^* = conversion rate of organic nitrogen to free and saline ammonia, $0{,}023(1{,}029)^{T-20}$ ℓ.mg $VSS^{-1}.d^{-1}$

N_a = ammonia concentration, mg NH_3-N. $^{-1}$. Additional subscript i refers to influent value

N_c = nitrification capacity, mg N.ℓ^{-1}

N_{ne} = effluent nitrate concentration, mg NO_3-N.ℓ^{-1}

N_o = organic nitrogen concentration, mg N.ℓ^{-1}

N_s = nitrogen requirement for sludge synthesis, mg N.ℓ^{-1}

N_{ti} = influent TKN concentration, mg N.ℓ^{-1}

P = COD:VSS ratio, 1,48 mg COD.mg VSS^{-1}

Q = influent flow rate, $\ell.d^{-1}$

R = nominal reactor retention time, h or d

R_a = actual retention time, h or d. Values marked ' refer to first phase of denitrification

R_h = hydraulic retention time, d

R_s = sludge age, d

s = underflow (sludge) recycle ratio

S_{bi} = biodegradable influent COD concentration, mg COD.ℓ^{-1}

S_{bsi} = readily biodegradable influent COD concentration, mg COD.ℓ^{-1}

S_f = safety factor

S_{ti} = total influent COD concentration, mg COD.ℓ^{-1}

t = time

T = temperature, °C. Subscripts min and max denote the minimum and maximum process temperatures, respectively.

V = process volume, ℓ

X = general parameter for sludge concentration, mg VSS. $^{-1}$. Subscripts a, e, i and v refer to active, endogenous, inert and total volatile concentrations, respectively.

Y_h = heterotrophic organism yield coefficient in terms of substrate as COD, 0,45 mg VSS.mg COD^{-1}

α = proportionality constant, mg N.mg COD^{-1}

ΔN_a = reactor nitrate removal, mg NO_3-N.ℓ^{-1}

ΔN_s = system nitrate removal, mg NO_3-N.ℓ^{-1}

μ_{nm}^* = maximum *specific* growth rate for nitrifiers, d^{-1}

* Additional subscripts T, 14 or 20 refer to the value at T, 14 or 20°C, respectively.

† Additional subscripts 1 or 3 refer to value in pre- or post-denitrification reactor, respectively.

REFERENCES

Arkley, M. and G.v.R.Marais (1981). Effect of anoxic mass fraction on sludge production and settleability in the activated sludge process. Res. Rept.No.W 40, Dept. of Civil Eng., Univ. of Cape Town.

Dold, P.L., G.A.Ekama and G.v.R.Marais (1980). A general model for the activated sludge process. Prof.Wat.Tech., 12, 47-77.

Downing, A.L., H.A.Painter and G.Knowles (1964). Nitrification in the activated sludge process. J.Proc.Inst.Sew.Purif., 64, 130-158.

Marais, G.v.R. and G.A.Ekama (1976). The activated sludge process Part 1 - steady state behaviour. Water S.A., 2, 4, 163-200.

Van Haandel, A.C., G.A.Ekama and G.v.R.Marais (1981). The activated sludge process - 3 : single sludge denitrification. Water Research (in press).

Van Haandel, A.C. and G.v.R.Marais (1981). Nitrification and denitrification kinetics in the activated sludge process. Res.Rept. No.W 39, Dept. of Civil Eng., Univ. of Cape Town.

Wat.Sci.Tech., 15, 3/4, 15-41, 1983

REVIEW: OBSERVATIONS SUPPORTING PHOSPHATE REMOVAL BY BIOLOGICAL EXCESS UPTAKE

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Abstract

The paper briefly reviews the development of the biological excess removal of phosphorus in the activated sludge process, from 1959 when it was first observed to the present. It concludes by proposing, tentatively, a biochemical mechanism whereby excess P uptake and release can be explained.

INTRODUCTION

From the first publication reporting phosphorus removal in excess of metabolic requirements in some activated sludge plants there has been controversy as to the mechanism whereby the excess removal is accomplished, whether the mechanism is a precipitation of inorganic compounds, albeit biologically mediated, *or* biological through metabolic formation and accumulation of phosphorus compounds in or on the organisms. This paper will discuss evidence that supports the hypothesis that excess phosphorus removal normally is via a biological mechanism. This does not imply that precipitation of inorganic phosphorus salts, due to chemical changes resulting from biological action, e.g. Alkalinity, Acidity and pH, does not take place. Such inorganic precipitation certainly can occur, but it would appear that in the treatment of municipal waste flows by an appropriately designed activated sludge process, within the normal ranges of pH, Alkalinity, Acidity and calcium concentrations in the influent, excess P removal is principally via a biological mechanism.

The types of evidence to be presented are of two kinds, direct and indirect. Direct evidence normally is explicit to the objective; whereas indirect evidence is inferred from behaviour analysed in terms of some hypothesis. However the fact that a particular hypothesis allows correct prediction of an outcome in a particular situation may provide support for the hypothesis, but does not constitute proof of it - other hypotheses may lead to the same prediction. Consequently an hypothesis gains credibility only by the consistency with which it predicts the outcome correctly over a spectrum of situations - much of the evidence favouring biological excess P removal is of the indirect variety.

The presentation is semi-historical; this not only provides a record of the evolution of a concept but also a convenient framework to evaluate the contributions of the various investigators.

CONCEPT EVOLUTION

Discovery

According to Levin and Shapiro (1965), it was Srinath, Sastry and Dilla (1959)

in India and Alarcon (1961) in America, who independently of each other, first drew attention to a phenomenon they observed in the activated sludge process: on occasion, removal of phosphorus (P) took place from the bulk liquid in excess of that indicated by normal metabolic requirements. These investigators concluded that in the plants where they observed excess removal, the magnitude of the removal appeared to be linked to the intensity of aeration. Tests on batches of mixed liquor indicated that if adequate aeration was provided, significant reductions in P, to near zero concentration were observed; however, if aeration was continued then with time a slow release of P back to the bulk of the liquid took place. Figure 1 shows the P uptake behaviour in a batch sample of mixed liquor under aeration, taken from Srinath *et al.* and is historic in recording the first evidence of biological excess P uptake in the activated sludge process.

Phosphorus Uptake and Release

The scientific father of *biological* excess P removal undoubtedly is Shapiro. In 1965 he and his pupil Levin reported on an extensive investigation into P uptake and release. As a basis for their investigation they went out from the hypothesis that the uptake is biological, mediated by the metabolic pathways normal to aerobic organisms, namely the sequence of the Embden-Meyerhof pathway and Krebs cycle, particularly the latter because P uptake takes place during aerobic conditions. Furthermore, they noted that in the literature it had been reported that some fungi, algae and bacteria stored phosphates in granular clusters called volutins; if P could be stored in this fashion then the carbon/phosphorus (C/P) ratio normal to microorganisms would not apply and excess uptake would find an acceptable explanation.

In their experimental investigation Levin and Shapiro (1965) obtained mixed liquor from the District of Columbia Sewage Treatment Plant, a "high rate" i.e. short sludge age plant. Samples aerated with, and without wastewater addition both exhibited P uptake, but the magnitude of the P uptake and its rate of uptake were *higher* for samples *with* wastewater addition than for ones without, indicating that the carbonaceous energy addition promoted uptake. If aeration was prolonged P release to the bulk liquid commenced, as previously observed by Alarcon (1961), indicating that the stored P was associated with the active fraction of the sludge - endogenous respiration reduces the active mass and the associated stored P will be released. In batch tests on two samples, of which one was aerated and the other not, the aerated one *took up* P while the unaerated one *released* P; this they

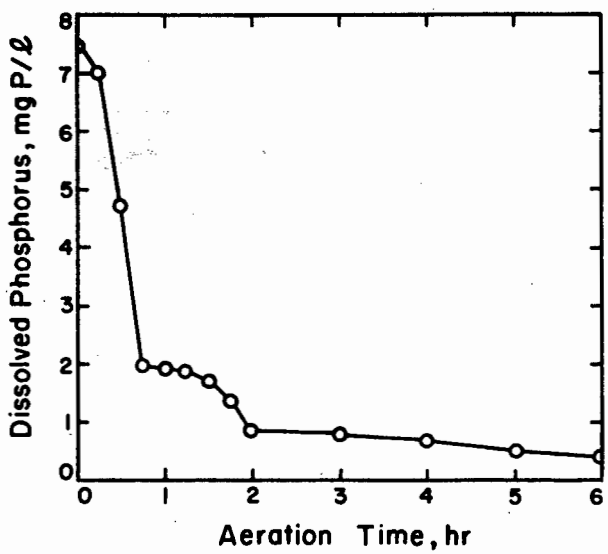

Fig.1. P uptake behaviour of a batch of mixed liquor from a plant showing excess P removal. (Taken from Levin ahd Shapiro of data reported by Srinath *et al.* 1959).

hypothesized could be explained by P uptake for ATP formation by *oxidative phosphorylation* in the (aerobic) Krebs cycle with oxygen as electron acceptor. In contrast the Embden-Meyerhof pathway, which remains operative under "anoxic" (anaerobic)* conditions, with *substrate phosphorylation*, did not appear to be implicated in the uptake because P was released under anoxic (anaerobic) conditions. However Levin and Shapiro offer no comment on the possible causes for the release. If the Krebs cycle is implicated in uptake then, they reasoned, (1) the oxygen tension in the mixed liquor and (2) poisons that inhibit oxidative phosphorylation (during aeration) should effect P uptake and they accordingly investigated these.

(1) Oxygen tension: Batch experiments at different aeration rates indeed showed that at low rates the P uptake rate was correspondingly low but as the aeration rate increased so uptake rate improved, but at a diminishing tempo to some plateau. From this it can be speculated that inadequate aeration should adversely affect P uptake but aeration beyond a certain rate would not lead to improvement in uptake. However, high aeration intensity should strip CO_2 and the consequential rise in pH may cause calcium phosphate to precipitate. To check if high aeration rate did not perhaps promote precipitation, Levin and Shapiro aerated five batches of mixed liquor in which the pH was controlled to remain at 5, 6, 7, 8 and 9, respectively. The results from the batches at the higher pH values are of particular interest: at pH 7 and 8 the uptake rate was rapid whereas at pH 9 the uptake rate was significantly *lower*. Normally one would expect that if precipitation was due to solid calcium phosphate formation, the rate would be higher at pH 9 than at pH 8; observing the opposite it was concluded that the mechanism was not precipitation.**

(2) Inhibition: With regard to the effects of poisons or inhibiting substances it is well known that 2,4-dinitrophenol inhibits oxidative phosphorylation.*** Levin and Shapiro found that on aerating mixed liquor samples with and without dinitrophenol, the sample *with* the phenol showed hardly any uptake whereas the sample *without* the phenol took up all the dissolved P. This indicated that when the Krebs cycle is inhibited P uptake does not occur suggesting that the mechanism is biological.

To Levin and Shapiro must be accorded the credit for hypothesizing a biological mechanism for P uptake and providing the first experimental data supporting this concept.

> The pioneering work of Levin and Shapiro has been verified and extended by a number of investigators. Sekikawa, Nishikawa, Okazaki and Kato (1966) found that the soluble phosphate in the bulk liquid increased if (i) there is a deficiency of "nutrients" (carbon energy) i.e. when the sample is aerated for a long period of time without COD a-dition; (ii) aeration is withheld i.e. anaerobic conditions are established and (iii) a poisonous substance such as K_2CrO_4 is added to the mixed liquor.****

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* The terms anoxic and anaerobic have acquired a usage in sanitary engineering that differs from that in bacteriology. In sanitary engineering anoxic implies absence of oxygen but presence of nitrate; anaerobic implies absence of both oxygen and nitrate. In bacteriology the term anoxic is not common and the term anaerobic implies absence of oxygen and includes the condition where nitrate is present. In this paper the sanitary usage will apply and when quoting from bacteriological papers the sanitary terms will be added in brackets after the bacteriological ones.

** There is evidence of a species of calcium phosphate precipitant with a low solubility product that forms at pH 7 to 8 but its rate of formation is extremely slow in the presence of organic material.

*** but not reductive phosphorylation.

**** These findings appear to have been obtained independent of Levin and Shapiro although this is not certain.

The inhibitory effect of 2,4-dinitrophenol on P uptake has been repeatedly duplicated by later workers, for example, Yall, Broughton, Knudsen and Sinclair (1970), Fuhs and Chen (1975) and Rensink, Donker and de Vries (1981). In general, in batch tests taken from the reactor showing release if the phenol is added at 1 to 2 mM/ℓ and aerated, either uptake is inhibited or there may be a release of P during aeration; this is dramatically illustrated by the plots in Fig.2 taken from Rensink *et al.*

The conclusion of Levin and Shapiro, that uptake is not physical-chemical, has been checked by a number of investigators:

(i) Yall *et al.* (1970) studied the removal of P by monitoring radio active ^{32}P and ^{45}Ca additions to their experiments. Their conclusions, *inter alia*, were that calcium phosphate precipitation played a minor role in the excess P uptake observed in their experiments.

(ii) Barnard (1976) in an experiment in which the pH in a Bardenpho process was raised, found no significant increase in excess P *removal** as would be expected if a physical-chemical mechanism was operative.

(iii) Hoffman and Marais (1977) set up two identical 2-reactor series configuration laboratory scale activated sludge plants, the one operated anoxic-aerobic, (i.e. nitrate was present in the anoxic zone), the other aerobic-aerobic, and ran batch tests on the mixed liquors from these plants: In the batch test on the aerobic-aerobic mixed liquor, by raising the pH to 7,3 and then lowering it to 6,0 they found that on raising the pH both the concentrations of Ca and P were reduced in the bulk liquid in the approximate molar ratio of [Ca]/[P] = 3 and on

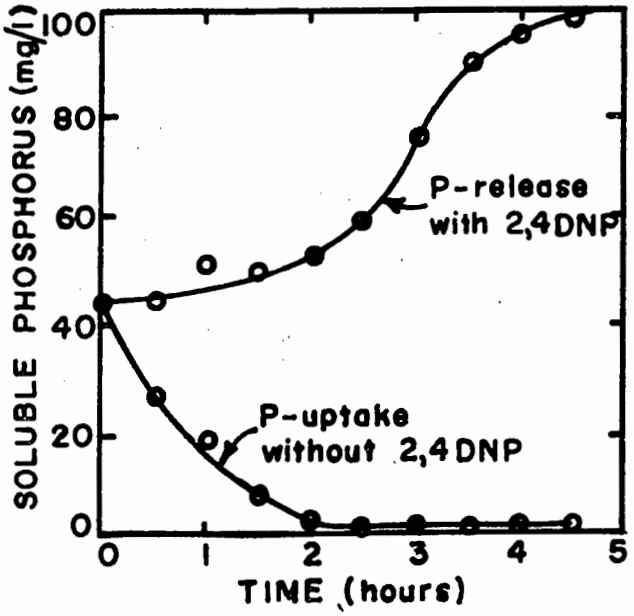

Fig.2. Effect of addition of 2,4 dinitrophenol on P uptake on aerating a batch that had been anaerobic. (Taken from Rensink *et al.* 1981).

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*In this paper *uptake* refers to the reduction in P in a batch test or in a reactor whereas *removal* refers to the reduction achieved by a continuous process, between the influent and the effluent. In a continuous process it is conceivable that in different reactors there can be *uptake* and *release* without *removal* being accomplished by the process.

lowering the pH, Ca and P increased again in the same ratio. They concluded that the phenomena probably were precipitation and dissolution respectively of a calcium phosphate mineral, although the Ca/P ratio did not conform to any of the commonly known calcium phosphate minerals. By making mass balances of P across the continuous processes, taking due account of P requirements for basic metabolic requirements and for precipitation as noted in the batch tests, it was possible to account for the P removal in the aerobic-aerobic system but not in the anoxic-aerobic system. The latter system always gave the higher P removal irrespective of whether the plants were run at pH 7,3 or 6,0 and the [Ca]/[P] always was very much less than 3. Furthermore it was noted at times that when the pH of a system was lowered suddenly from pH 7,3 to 6 the Ca concentration in the effluent temporarily could exceed that of the influent and concomitantly the P removal temporarily was reduced; this behaviour pattern indicated that calcium phosphate that had precipitated at the higher pH, dissolved at the lower pH. In general however, for this influent (low Alkalinity and Ca = 40 mg/ℓ) calcium phosphate precipitation at pH 7 could account for only about 1 mg P/ℓ removed; the major removal was judged to be due to the biological excess phenomena.*

(iv) Rensink *et al.* (1981) clearly demonstrated the complete lack of association between Ca and P in plants giving excess P removal attributable to the biological mechanism. They operated a 10 in-series reactor activated sludge plant with the first 5 reactors not aerated and the underflow recycle discharging to the first reactor. The plant was operated at a low sludge age of 5,3 days, at 14°C, and no nitrification was observed so that the first 5 reactors were anaerobic. Plots of the concentrations of phosphorus, calcium and magnesium in the bulk liquid are shown in Fig.3. Evidently the increase and decrease of soluble P was completely independent of the concentration of Ca so that the behaviour cannot be ascribed to dissolution and precipitation of phosphate minerals.

In 1967 Shapiro, and Shapiro, Levin and Zea (1967) focussed attention on the P release aspect under anaerobic conditions. They (1) verified the earlier findings of Levin and Shapiro (1965) that although there was P uptake during aeration, P was again released during "anoxic" (anaerobic) conditions, i.e. uptake and release were reversible; (2) found that the release apparently was triggered by a lack of oxygen and/or a low redox potential, but, of these two they concluded that release appeared to be controlled more by the redox potential than the oxygen tension - Shapiro observed that rapid release appeared to be triggered off once the redox potential fell to -150 mV; (3) found that in batch tests the P appeared to be released from the acid-soluble fraction of the sludge cells and to a minimal degree from the RNA and DNA protein fractions, in general the total protein was hardly affected; (4) found that during anaerobiosis, apart from the observed P release, the BOD of the liquid medium hardly changed, soluble TKN also showed no change for the first 40 minutes but thereafter increased rapidly, mostly in the NH_3 form. The behaviour of these three parameters during a batch test is plotted in Fig. 4.

There are several aspects of the above observations that merit discussion -

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*It is of interest here to note that irrespective of whether the conditions in the "anoxic" reactor are anaerobic or anoxic some excess P removal always will be obtained. Generally if the system is aerobic-aerobic the P concentration in the *active mass* is about 3 percent, if anoxic-aerobic about 6 percent and if anaerobic-aerobic (provided a number of other conditions are satisfied, see later) can range from 6 to 35 percent. The concentration of P in *endogenous residue* and in *inert volatile* material in the influent, is about 1,5 percent.

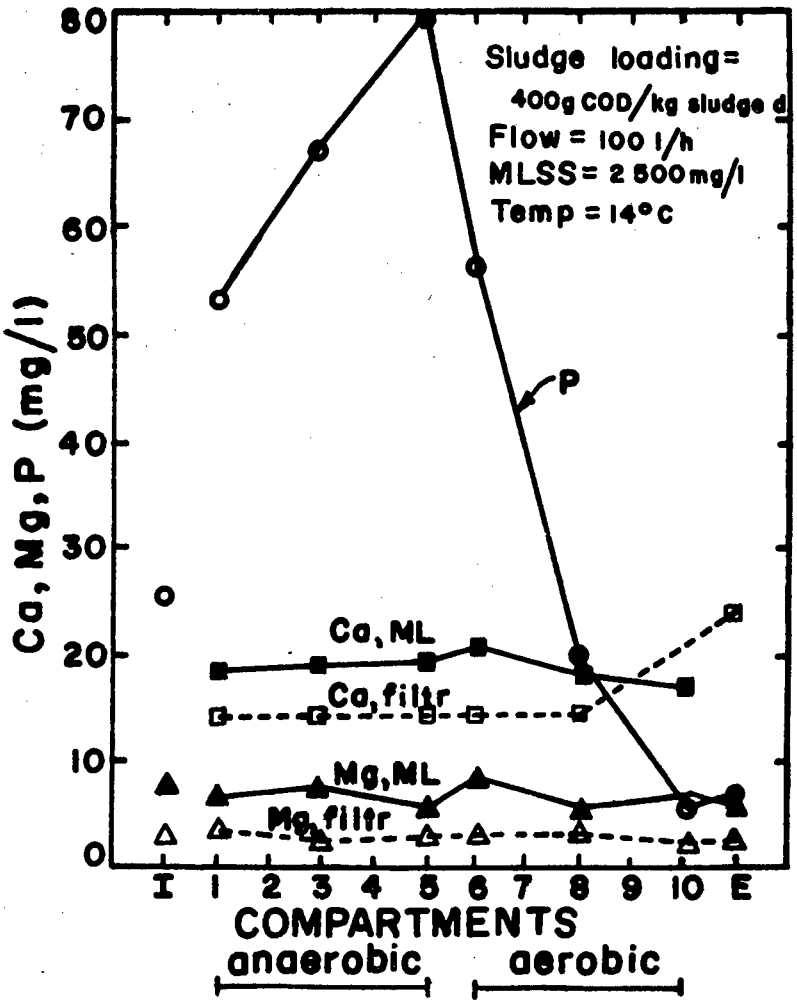

Fig.3. P and Ca behaviour in a 10 series reactor system with the first 5 reactors anaerobic to illustrate lack of association of P and Ca. (Taken from Resink *et al.* 1981).

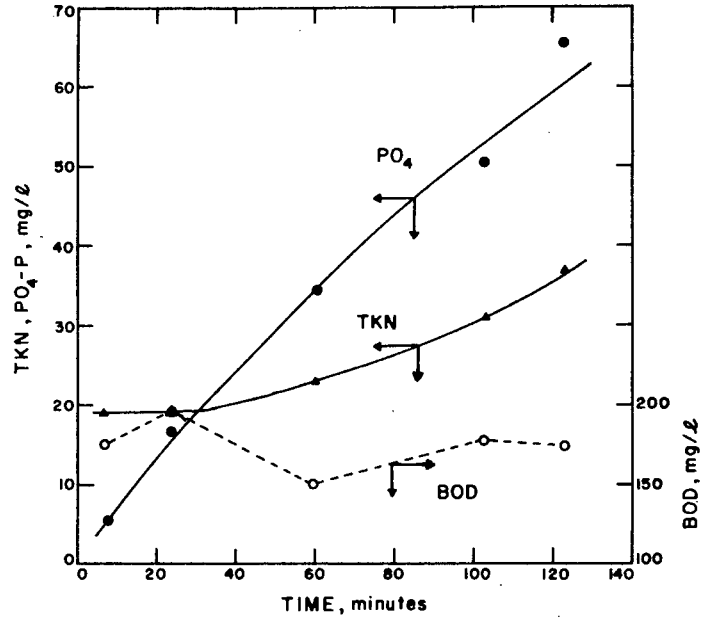

Fig.4. Changes in soluble BOD, TKN and P in a batch under unaerated conditions. (Taken from Shapiro, 1967).

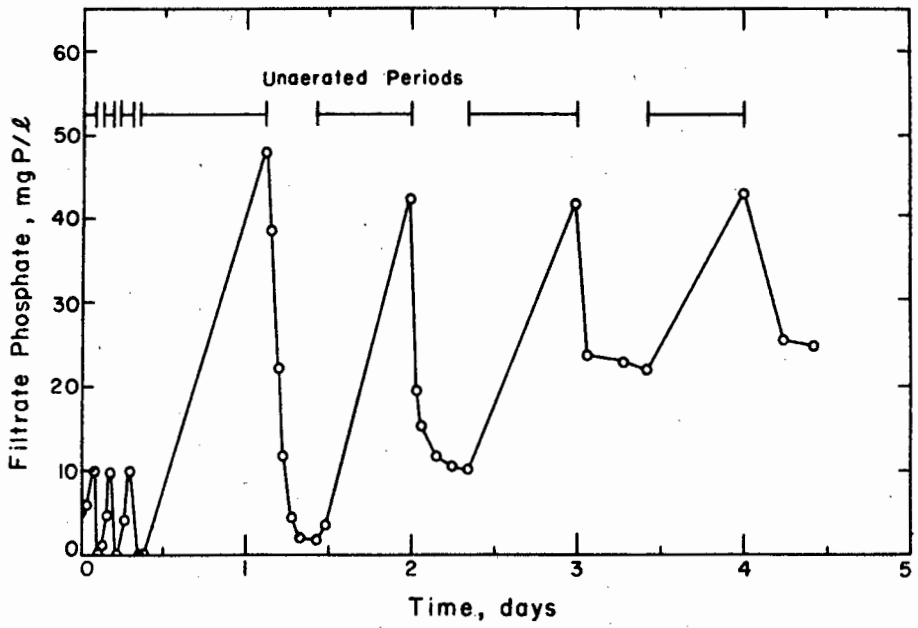

Fig.5. Phosphorus uptake and release in a batch test under alternating aerated and unaerated periods. Sludge sample taken from a high rate plant (after Wells,1969).

(i) Reversibility of uptake and release: Wells (1969) using batches of mixed liquor from the San Antonio plant (which exhibited P removal) verified that if a batch is sequentially aerated during the day and left unaerated during the night, phosphorus was taken up during the day and released during the night, but, that the uptake decreased progressively (Fig.5). If one plots the P uptake each day versus the relative active mass for that day, calculated by means of the activated sludge kinetic theory of Dold, Ekama and Marais (1981), one has the interesting result that the uptake appears to be linearly related to the active mass - a behaviour pattern more in keeping with biological mechanism than a physical-chemical one, and indicating that the biological uptake is limited by the active mass even though the factors controlling the magnitude of the uptake are not identified (see Fig.6).

(ii) Redox potential and oxygen: Redox potential as parameter controlling P release has a deceptive persuasiveness about it. In samples from long sludge age plants, P is not immediately released when dissolved oxygen becomes zero, release may only commence after a considerable time has elapsed. In contrast, in samples spiked with influent, release is virtually immediate when the dissolved oxygen becomes zero. Consequently, the reasoning is that it is not the dissolved oxygen *per se* but the redox potential that needs to be depressed to a sufficiently low value before P is released even though the mechanism of release is not described. Barnard (1975a) and Siebritz, Ekama and Marais (1980) followed Shapiro *et al.* in accepting this explanation for P release. In order to test this hypothesis, one problem is that reliable measurement of redox potential in biological systems is difficult; as a consequence the hypothesis has not been conclusively proved or disproved. To bypass the difficulties with direct measurement, Siebritz *et al.* (1980) substituted the redox potential by a parameter called the anaerobic capacity; this parameter is defined as the mass of nitrate that can be removed in an anaerobic reactor if sufficient nitrate is available. From this definition the anaerobic potential is an extensive parameter whereas redox potential is an intensive one; replacing the redox potential by the anaerobic potential is analogous to replacing pH by the total alkalinity. Such a replacement is allowable for pH under

restricted conditions only and this will be true also for the redox potential, but the conditions which allow such a substitution are not clear. However Siebritz, Ekama and Marais (1980) found that the anaerobic capacity was not a consistent parameter and was only of restricted use in predicting P release. (see later).

Randal, Marshall and King in 1969, specifically investigated the connection between redox potential and P release and concluded that there is no evidence supporting the hypothesis that the redox potential controls the release. From spiked batch tests they found that in all cases but one, release always took place immediately the dissolved oxygen became zero, but a reduction in the redox potential lagged by about 40 to 60 minutes; they concluded that the redox potential is only weakly linked to P release. The late changes in redox potential, observed by Randal *et al.* very likely are due to the commencement of "fermentation", in which CO_2 or perhaps H^+ in the bulk liquid commences to serve as electron acceptor and thereby giving rise to a change in the redox potential evident in the bulk liquid - it would appear that the causes for P release must be sought *inside* the organism, as will be discussed later.

(iii) Insensitivity of soluble BOD: The insensitivity of the soluble BOD under anaerobic conditions as reported by Shapiro is not unexpected. Dold, Ekama and Marais (1980) in their death-regeneration model for bacterial metabolism concluded that during death of organisms the lysed products are *particulate* and become enmeshed in the sludge mass or adsorbed onto the active mass fraction; consequently these products will not be reflected in a COD or BOD test conducted on a filtered sample. The fact that Shapiro reported that in the filtered supernatant the NH_3 increased after about 40 minutes (Fig.4) indicates that the particulate TKN (or protein) set free by the death and lyses of the organisms commenced to be broken down to NH_3 by anaerobic action, and/or direct anaerobic destruction of some organism started to occur due to a qualitative shift in the population from facultative to anaerobic -

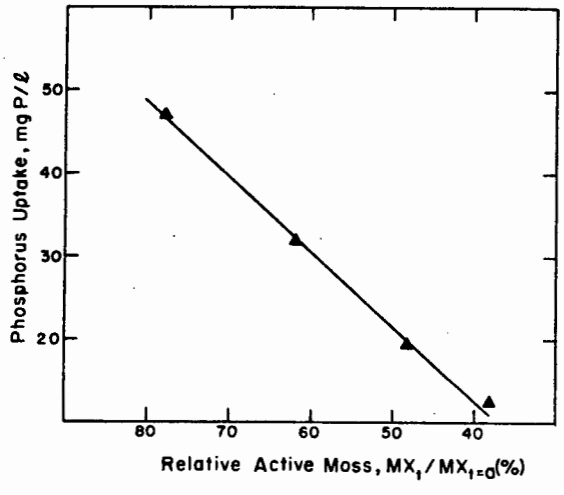

Fig.6. P uptake versus relative active mass as a percentage of the initial active mass as from the batch test results shown in Fig.5.

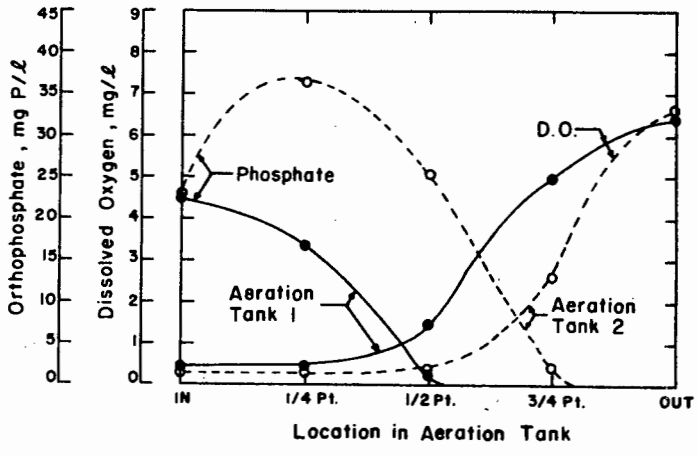

Fig.7. Typical orthophosphate and dissolved oxygen concentration profiles along the length of a full scale plug flow activated sludge process (after Scalf *et al.*,1969).

an explanation not inconsistent with the late changes in redox potential observed by Randal *et al.*

Subsequent research by Shapiro and Levin was oriented to the development of their Phostrip method and does not contribute materially to the development of the biological excess P removal concept.

Phosphorus accumulating organisms

In 1975 Fuhs and Chen presented the results of an intensive investigation into excess P removal undertaken from 1973. It would appear that they went out from the hypothesis that (1) if excess removal is biological then some organism(s) in the sludge mass must be capable of accumulating the phosphorus, and (2) an anaerobic-aerobic sequence is important in some, as yet, undefined manner.

In preliminary work they utilized an aerobic activated sludge laboratory unit which had been run for a number of years on an artificially constituted influent substrate. They converted the operation to run on an anaerobic-aerobic cycle for two weeks but could obtain no evidence of excess P removal. On examining the organisms in the sludge microscopically after suitable straining they concluded that this behaviour was not unexpected as only few of the organisms in the mass were capable of storing polyphosphates. Thereupon they studied samples of activated sludge from the Black River Treatment Plant of Baltimore and the Seneca Falls Plant as both these plants exhibited excess P removal. The samples of sludge were stored unaerated the night after collection and the following day unsettled influent from the respective plants was added to the respective batch samples of sludges, and aerated for 4 hours. (The reported mass of sewage added indicated a very high COD load per unit mass of sludge). A dramatic decrease in phosphorus, from about 32 to near zero mg P/ℓ, was observed over the 4 hours. Subsequent storage of the batch unaerated for 20 hours caused release to about 40 mg/ℓ. Parallel tests, in which the one test sample was spiked with 2 mM/ℓ 2,4-dinitrophenol, indicated virtually complete inhibition of the uptake mechanism during aeration. Microscopic examination of the sludge mass during aeration indicated the presence of intercellular accumulations of inorganic polyphosphates in some bacteria; during the subsequent 20 hour anaerobic period the inclusions disappeared and the P in the bulk liquid increased. Repeated cycles of aeration (4 h) and anaerobiosis (20 h) indicated that uptake and release were associated; when P release was high so was the subsequent uptake, when P release was indifferent or zero (even after 20 h of anaerobiosis) so also was the subsequent uptake. Generally P release and uptake decreased as the number of cycles increased.

Microscopic study of the P accumulating organisms indicated that the accumulations were specific to one morphological bacterium type. From a series of identification tests Fuhs and Chen concluded that the organism associated with the phosphorus accumulations belonged to the *Acinetobacter* genus. Pure batch cultures of this organism fed on acetate when subjected to the anaerobic-aerobic cycle gave rise to a behaviour pattern very similar to that with the mixed liquor sludge samples. By the third cycle no release was obtained during the anaerobic period and under the subsequent aerobic period a slow release was observed. However when acetate was added during the final aerobic period, rapid uptake of P again took place.

The eventual slow release even under aerobic conditions is not unexpected; elsewhere it has been noted, in Fig. 5, that the uptake and release decrease as the number of cycles increases. If continued long enough then, consistently, little or no release and uptake should be observed within the cycle sequence; the release under aerobic conditions then could be accounted for by a greater loss of P due to endogenous conditions than due to excess uptake. With regard to the P uptake on addition of acetate, if one accepts that release and uptake are linked, as surmised by Fuhs and Chen, then the uptake finds explanation in that the preceding anaerobic period "conditioned" the sludge mass for uptake when a carbon energy source became available. (It

should be noted that the P uptake on acetate addition is possibly magnified due to the pure culture organism mass; in mixed cultures the effect would be much smaller due to competition for the acetate by other organisms).

Assessing Fuhs and Chen's work the following important aspects must be credited to them: (1) Although not explicitly stated they were the first to surmise a possible link between P release and subsequent P uptake; (2) they implicated an organism group, the *Acinetobacter* genus, as responsible for the P uptake and release; (3) they suggested that the growth of the *Acinetobacter* was as a result of the anaerobic-aerobic sequence; in their own words "Anaerobic conditions preceding aerobiosis in sewage treatment .... could well be related to the appearance of *Acinetobacter*", and (4) they speculated on a biochemical model that explained the growth of the *Acinetobacter* in a more explicit fashion than Shapiro. Again in their own words: "The principal function of the anaerobic treatment .... is to establish a facultatively anaerobic microflora. .... During anaerobiosis this flora would tend to produce compounds such as ethanol, acetate and succinate which serve as carbon source for *Acinetobacter* .... without anaerobiosis, an obligately aerobic assemblage is likely to develop; and the intermediate products would not be formed. *Acinetobacter*, which cannot attack sugars* or polysaccharides and are likely to be subject to heavy competition for the utilization of amino acids, would not then develop." Their proposed mechanism (4 above) however is open to reservations: Their argument, that the function of the anaerobic period is to produce intermediates which can be utilized by the *Acinetobacter* in the aerobic phase, does not explain why the *Acinetobacter* appear to grow preferentially in anaerobic-aerobic system - these organisms on entering the aerobic phase would still be subject to the same competition with other organisms as if these intermediates were added from external sources to an aerobic system. Their argument also does not explain why an anaerobic-aerobic sequence appears to be essential for P uptake. Under steady state aerobic conditions Harold (1966), for example, found that *Aerobacter Aerogenes* (an organism that also can accumulate phosphorus) accumulated P only minimally, so that it would appear that some stress situation in the anaerobic-aerobic cycle triggered the P release and uptake. However despite these unresolved questions Fuhs and Chen did clearly demonstrate that the cycles of anaerobic-aerobic phases gave rise to a sludge with specific organisms for P uptake and release, even though the reasons for this remained unknown.

It is of interest to note that in 1967 Wells already came to the conclusion that the sludge in plants giving excess P removal differed from those in plants that did not. He states: "The rapid uptake of phosphates by the Rilling Road plant sludge and the almost complete absence of uptake by the East and West plant sludges when treated under identical conditions, indicate a fundamental difference in the nature of the sludge itself over and above plant differences which produced the sludge".

Osborn and Nicholls (1977) pointed out that besides *Acinetobacter* a large number of organisms capable of accumulating P have been reported in the literature. Furthermore in P removal plants, as designed in South Africa, it has been repeatedly observed that considerable P is taken up in the *anoxic* reactor receiving the outflow from the anaerobic reactor; *Acinetobacter* being an obligate aerobe should find the anoxic reactor quite unfavourable for growth thereby suggesting that the facultative denitrifying bacteria might also include P accumulating organisms and play a role in P removal.

Despite the difficulties in explaining the presence of the *Acinetobacter*

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*For example, *Acinetobacter* cannot utilize glucose, a most readily biodegradable substrate.

there is little doubt that this organism is an important one in P excess uptake. Osborn and Nicholls (1977) studying activated sludge plants in the Johannesburg area noted the presence of *Acinetobacter* type organisms in all the plants having an anaerobic zone. Rensink *et al.* (1981) found the P accumulating organisms increased under anaerobic-aerobic plant operation with consequential increases in P removal.

Buchan (1981) investigated the morphology of the phosphate-accumulating organisms and the chemical composition of phosphorus accumulates. From mixed liquor samples taken from the Brits, Goudkoppie, Umhlatuzana and laboratory scale units all showing excess P removal, he positively identified that these processes all contained organisms of the *Acinetobacter* group. To investigate whether this bacterium group is in fact able to accumulate large amounts of phosphorus, he grew pure cultures of species of this group under batch test conditions. His results indicated that the *Acinetobacter* can accumulate P in excess of 30% of the organism mass. Ohsumi, Shoda and Uduka (1980), Shoda, Ohsumi and Uduka (1980) and Lawson and Tonhazy (1980) all investigated pure cultures of the *Acinetobacter* group and all found that the group can accumulate phosphorus in excess of 20 percent by mass.

Lawson and Tonhazy (1980) and Buchan (1981), utilizing a scanning electron microscope confirmed the findings of Harold (1966) that metachromatic cell clusters (volutin) were rich in phosphorus. Buchan noted a consistent association of phosphorus and calcium in the phosphate-rich inclusions indicating that calcium may be an essential requirement for biological phosphate accumulation so that calcium is important not only for inorganic calcium phosphate precipitation but also for biological excess P uptake.

Phosphorus Release Prerequisite

In the late 1960's and early 1970's considerable data were collected on full scale plants exhibiting excess P removal, for example, by Vacker, Connel and Wells (1967), Scalf, Pfeiffer, Lively, Witherow and Priesing (1969), Witherow (1970) and Millbury, McCauley and Hawthorne (1971). All these plants were of the conventional type i.e. with long plug flow reactors, graduated aeration from the inlet to outlet, and all were operated under high loading rates or equivalently very short sludge ages, from 1½ to 6 days. Underflow recycle ratios (where these are given) ranged from 0,25:1 to 0,5:1, Dissolved P profiles along the reactor axis characteristically showed P values well in excess of those in the influent near the influent end (indicating release) up to the point where the oxygen concentration becomes positive, whereafter there was a rapid drop in P (indicating uptake) up to the effluent end, see Fig.7. It was generally accepted that the release was due to a lack of oxygen arising from the high oxygen demand near the influent end, but no special significance was attached to this beyond the possible reduction in P removal by the process if release should commence in the secondary clarifier. The reports principally focussed attention on the uptake of P, and in particular the effect of aeration intensity at the effluent end on the rate of uptake; Milbury *et al.* for example noted that reverse aeration, i.e. higher intensity aeration at the effluent than at the influent end produced improved P removal. However, the plug flow rêgime *per se* was recognized as conducive to uptake and Milbury *et al.* accordingly recommended length: width ratios of 25:1 in design of the reactor. Step feeding to the reactor positively was to be avoided; when operated with step feeding Milbury *et al.* observed a rapid loss of the P removal propensity. As step feeding provides a mixing rêgime approaching that of complete mixing, completely mixed rêgimes accordingly also were not recommended. A further observation of note was that the filtrate of digested sludge from these plants needed to be treated to remove P prior to returning it to the head of the works for further treatment: if this was not done the plants lost their P *removal* propensity even though *release* and *uptake* continued as

before. This observation is important in that it indicates that the sludge has a limited P accumulation propensity, an observation that lends support to the biological as against the physical-chemical excess P uptake hypothesis.

The observations on the behaviour of these full scale plants were of significant importance in the evolution of the excess P removal concept. Descriptions of the plant behaviour generally displayed sharp insight; although they did not immediately lead to basic solutions, they influenced all subsequent investigations and served, and serve still, as measures against which various hypotheses on excess P removal can be evaluated.

The first surmise that P release may be a prerequisite to excess P uptake was, as we have seen in the previous section, due to Fuhs and Chen. However it is to Barnard (1975, 1976) that an explicit statement to this effect is due. He hypothesized that, for excess P uptake, the mixed liquor needs to be subject to an anaerobic state at some point in the process of such intensity that P release is obtained, then, if the mixed liquor is adequately aerated, P uptake in the aerated reactor, and P removal by the process, will be obtained. Barnard came to this hypothesis while testing a 4 reactor Bardenpho (nitrification-denitrification) pilot plant with nominal reactor retention times of 2 h primary anoxic, 6 h aerobic, 3 h secondary anoxic and 1 h reaeration respectively, operated at an unspecified long sludge age with a 4:1 mixed recycle ratio and 1:1 underflow recycle ratio. With an influent total P concentration of 9 to 12 mg/ℓ he noted that the filtered P in the 4 reactors typically were 2,5; 2,5; 30 and 0,3 mg/ℓ indicating a massive release in the second anoxic reactor and a massive uptake in the reaeration reactor.* He also established that the magnitude of the P removal was very adversely affected by nitrate; as nitrate in the effluent increased so the P removal declined. The confounding effect of nitrate first noted by Barnard henceforth was to be a constant source of difficulty in all investigations into nitrification-denitrification-P removal processes.

From the background of the experiment above, and after reviewing the literature Barnard (1976) stated "The foregoing discussion leads to the inevitable conclusion that the activated sludge returned from the clarifier or the mixed liquor must pass through an anaerobic phase where the oxygen demand exceeds the supply of both oxygen or nitrates at some stage except the final stage before clarification at which point it should be aerated. In this anaerobic zone or stage, a certain degree of anaerobiosis or a certain minimum level of the oxidation-reduction potential must be reached. At this level of the oxidation-reduction potential phosphates will be released to the liquid in the form of dissolved ortho-phosphates and whereas it would be difficult to measure the oxidation reduction potential, it would be a simple matter of control to measure the release of phosphates in the anaerobic zone as a means of ensuring that the necessary conditions for the removal of phosphates would prevail." Referring to previous reported investigations on high rate P removal plants in America he was "... led to the conclusion that the only common feature of all the plants that could be responsible for removal of the phosphates was the intentional or unintentional creation of an anaerobic zone in the plant as opposed to an anoxic zone. The sludge or mixed liquor passing through this anaerobic zone would then release phosphate to solution in the form of orthophosphates."

To achieve the prerequisite low redox potential for P release most expeditiously he proposed the Phoredox process, Fig.8. He modified the Bardenpho process by introducing an anaerobic reactor ahead of the first anoxic reactor to receive the underflow recycle and the influent waste flow. It was hypothesized that the waste organic load entering the anaerobic reactor would create the necessarily low redox potential for P release, furthermore, the Bardenpho section of the plant would reduce the nitrate sufficiently low that any nitrate in the underflow would have negligible effect on attaining the required low redox potential level in the

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*Curiously enough, in all subsequent reports by several investigators no P release has ever been reported in a secondary anoxic reactor even if no nitrate were present.

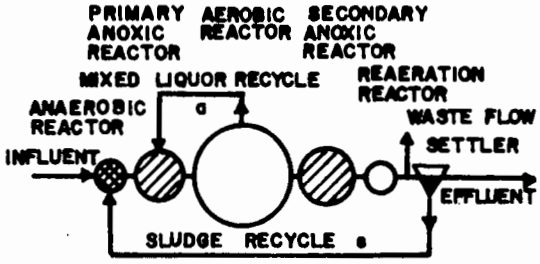

Fig. 8. The Phoredox process.

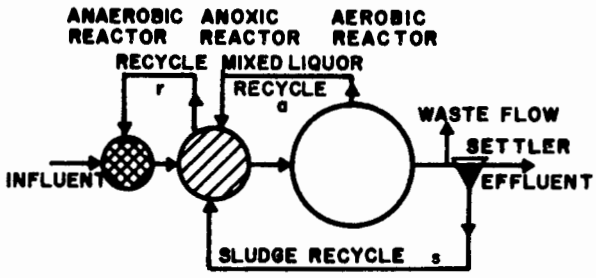

Fig. 9. The UCT process.

anaerobic reactor.

Barnard's proposed process and his P release hypothesis was experimentally investigated by a number of research workers, McLaren and Wood (1976), Nicholls (1977), Simpkins and McLaren (1978) and Davies and Wiechers (1978). These investigations verified that P release led to P uptake and P removal in the Phoredox process. Also it was observed that the magnitude of the removal appeared to increase with increase in the nominal retention time of the anaerobic reactor, that the denitrification in the secondary anoxic reactor per unit volume was relatively inefficient compared to the primary anoxic reactor and that nitrate in the underflow recycle had a pronounced adverse effect on excess P removal by the process. The inefficiency of the secondary anoxic reactor prompted Simpkins and McLaren to suggest that this reactor could be left out under certain circumstances and the primary anoxic reactor appropriately enlarged, to give the Modified Phoredox process.

Stern and Marais (1974), Martin and Marais (1975), Marsden and Marais (1976), Ekama, van Haandel and Marais (1979), Siebritz, Ekama and Marais (1980), Van Haandel, Ekama and Marais (1981), and Van Haandel, Dold and Marais (1982) focussed attention particularly on the denitrification aspects of the Bardenpho and Phoredox processes. They found that it was not possible to increase the anoxic zones in these processes *ad lib* in order to ensure low nitrate in the effluent and underflow recycles; if, for a selected sludge age and temperature the unaerated mass fraction of the sludge was increased beyond a certain magnitude, the process stopped nitrifying. They showed that the maximum anoxic mass fraction allowable was determined by the maximum specific growth rate of the nitrifiers, μ_{nm}, at the lowest temperature the process would be required to operate, and the sludge age. Limiting the anoxic mass fraction (to ensure nitrification) necessarily limits the magnitude of the denitrification achievable. They developed equations whereby the denitrification can be estimated and concluded that the Phoredox process can be designed to achieve nitrification *and* complete denitrification only if the TKN/COD (mg (TKN-N)/mgCOD) ratio of the influent is below about 0,08. For TKN >0,08 the nitrate concentration in the effluent and hence in the recycle to the anaerobic reactor increases causing a disproportionate decrease in the P removal. Usually the TKN/COD ratio of raw sewage is in the range 0,06 to 0,08 and for settled sewage 0,09 to 0,11; the 0,08 upper limit for the Phoredox process severely restricts the application of this process.

Siebritz, Ekama and Marais (1980) and Rabinowitz and Marais (1980) thereupon investigated modifications to the Phoredox process that would make the anaerobic reactor *independent* of the effluent nitrate concentration; this lack of independence, they perceived, was the main obstacle to developing a viable process suitable to treat high TKN/COD ratios. Their efforts led to the development of the University of

Cape Town (UCT) process, see Fig. 9. The underflow return discharges to the primary anoxic reactor (instead of the anaerobic reactor) and a further recycle (r-recycle) is introduced from the primary anoxic reactor to the anaerobic feactor; the secondary anoxic zone is left out so that the system contains 3 reactors only, anaerobic, anoxic and aerobic in series. By appropriate operation of the a-recycle the nitrate in the anoxic reactor can be maintained at approximately zero, and consequently, the anaerobic reactor receives a nitrate free recycle irrespective of the nitrate concentration in the aerobic reactor and effluent. This situation theoretically can be maintained for TKN/COD ratios up to about 0,14. Extensive experimentation (Siebritz, Ekama and Marais 1980, 1982) has confirmed that the UCT process can always ensure zero nitrate flow to the anaerobic reactor for TKN/COD < 0,14. Surety of a nitrate free recycle to the anaerobic reactor allowed a rational attack on the excess P removal phenomenon without having to contend with the confounding effect of the nitrate on the anaerobic reactor.

The importance of Barnard's contribution lies in his (1) recognition of a link between phosphate release under anaerobic conditions and subsequent uptake under aerobic conditions, (2) hypothesizing a process configuration which has the propensity to remove both nitrogen and phosphorus. This latter contribution is all the more significant for it required moving outside the ambit of the then existing activated sludge practice from, low sludge ages to long sludge ages, series plug flow reactors to completely mixed series reactors that include anaerobic, anoxic and aerobic reactors that allow nitrification and denitrification. His contribution can be said to have given a new direction to waste water treatment.

Readily Biodegradable Substrate Hypothesis

Barnard's hypothesis, that biological excess P uptake requires an anaerobic condition such that P release is obtained, is not helpful in design for it does not provide guidance as to how the required "intensity" of the anaerobic state can be predicted. The difficulties in this regard led him to suggest an empirical guideline - the anaerobic reactor should be provided with nominal retention time of about one hour; presumably this would reduce the redox potential to the level necessary to give P release. A further difficulty in design is that no guidance is given to predict the mass concentration of P that the system will remove in a given design situation. In fact, it was not possible to give any firm assurance, at the design stage, that the plant would in fact fulfil its design expectations. These difficulties are present to various degrees in sanitary engineering design and are to be expected in development of a new and rather novel process - they are symptomatic of a lack of a model that links the performance of the plant to some measureable input parameters. Research efforts towards resolving the process designer's problems now will be reviewed.

In developing a general model for the activated sludge process the University of Cape Town group established that normal municipal influents contain two biodegradable COD fractions, a readily biodegradable soluble and a slowly biodegradable particulate fraction (Dold, Ekama and Marais, 1980). They found that the denitrification behaviour of the plant was crucially affected by the magnitudes of these two fractions. When the influent readily biodegradable COD, S_{bsi}, entered the primary anoxic zone it was rapidly metabolized, in a few minutes, with the nitrate proportional to the mass of S_{bsi}. In contrast the influent slowly biodegradable COD, S_{bpi}, gave rise to a long term low rate reduction of nitrate. In the second anoxic reactor only the particulate COD, derived from the influent but principally from death and lysis of the organism mass, was operative. These effects gave rise to a two phase denitrification behaviour in the primary anoxic reactor and a single phase in the secondary anoxic, see Fig. 9. It was also observed that where an anaerobic reactor preceded the primary aerobic reactor the readily biodegradable COD in its passage through an anaerobic reactor (if no nitrate was introduced) apparently was

not affected and gave rise to the same reduction in nitrate in the primary *anoxic* reactor as if the anaerobic reactor were not present. It was further established that for every mg of nitrate reduced by the readily biodegradable COD, 8,6 mg of readily biodegradable COD was utilized, for synthesis and energy production. In the anaerobic reactor, therefore, entry of say 10 mg (NO_3-N) removed 86 mg readily biodegradable COD.

Van Haandel, Ekama and Marais (1981) extended the general aerobic model to incorporate the kinetic behaviour of the process under anoxic and anaerobic conditions and derived steady state equations by means of which the denitrification behaviour of a plant can be readily predicted. This in turn opened up a way to quantify the anaerobic state in the anaerobic reactor: Siebritz, Ekama and Marais (1980) proposed a parameter, the anaerobic capacity, which is defined as the difference between the denitrification potential of an anaerobic reactor and the nitrate discharged to the reactor where the denitrification potential is the maximum mass concentration of nitrate that the reactor can remove if sufficient nitrate is discharged to it. It was hoped that this parameter, because it could be estimated from the process kinetics and the input data, would substitute for the redox potential, which could not be predicted. Accordingly it was hypothesized that if the anaerobic capacity reached a sufficiently great magnitude, then P release would be induced in the anaerobic reactor.

Application of the anaerobic capacity to the UCT process indeed appeared to indicate that if the potential exceeded about 10 mg (NO_3-N)/ℓ in the anaerobic reactor then P release was observed with associated P removal. However when applied to a two reactor nitrification-denitrification system, Fig. 10, with an unaerated mass fraction of up to 70 percent, operated such that the anaerobic capacity was 34 mg/ℓ, no release in the first reactor was obtained and only minimal P removal by the process was achieved. In contrast a UCT process operated in parallel, with only 7,5 percent anaerobic mass fraction and an anaerobic capacity of 12 mg (NO_3-N)/ℓ gave rise to P release and excess P removal. The only evident difference between the two systems was that in the UCT process an appreciable concentration of readily biodegradable COD was present in the anaerobic reactor whereas in the two reactor process the nitrate recycled to the first or anaerobic reactor had completely utilized the readily biodegradable COD, so that the anaerobic capacity arose totally from the utilization of slowly biodegradable COD. These observations led to the hypothesis that the presence of readily biodegradable COD in the anaerobic reactor induced P release and excess removal.

Extensive research into the utility of this hypothesis over a year by Siebritz, Ekama and Marais (1982) established that release is induced if the readily biodegradable COD *in* the anaerobic reactor, S_{bsa}, exceeds about 25 mg/ℓ, the release and excess removal increasing as (S_{bsa}-25) increases. This opened the way for enquiry into other factors affecting the release and excess removal, and quantitisation of the excess removal. It appeared that excess P removal depended on (1) (S_{bsa}-25), (2) the fractional mass of sludge in the system passing through the anaerobic reactor, and (3) the actual time a unit of sludge is retained in the anaerobic reactor; if any one of these is zero, no excess removal is obtained. Empirically these three factors were combined in a *phosphorus removal propensity factor* and it was found that the fractional mass of phosphorus relative to the active mass, γ, could be functionally related to the P removal propensity factor.* Further investigation showed that in the Phoredox and UCT processes, due to the recycle systems and their interactive effects on the anaerobic retention time, the fractional mass of the sludge in the process passing through the anaerobic reactor per day and the concentration of S_{bs} in the anaerobic reactor, the three parameters can be reduced to two, (1) (S_{bs}-20) and (2) the *anaerobic mass fraction*, defined by (mass of

*Once γ is available the removal can be calculated from the sludge wasted each day, for, under steady state operation the *removal* can only take place via the waste sludge.

sludge in the anaerobic reactor)/(total mass of sludge in the system).

Extensive testing of the concepts embodied in the P removal propensity factor has, in every instance, verified the utility of this approach. At laboratory scale, employing the UCT process the concepts were tested at different sludge ages, temperatures, anaerobic mass fractions, influent COD concentrations in which the readily biodegradable fraction of the influent (unsettled municipal sewage) was augmented by addition of glucose or acetate. All these tests have given results remarkably consistent with the predictions of the theory. At full scale, in a joint research project with the Johannesburg City Council, on the Goudkoppies and Northern Works, analysis of the process in terms of these concepts has explained the poor and erratic P removal obtained in these plants and provided a basis for suggesting procedures to improve the removal where this was possible (Nicholls, Osborn and Marais, 1982). It would seem that the readily biodegradable hypothesis and its consequences allow for the first time, a rational quantitative approach to optimal design of proposed P and N removal plants, and a basis for evaluating the performance of existing plants (Ekama, Siebritz and Marais, 1982).

Biochemical Mechanism for P Release and Uptake

The models for excess P removal presented by Barnard and by Marais and his group are virtually totally heuristic because the behaviour is not explained in terms of, or directly linked, to any basic biological or biochemical phenomena, except perhaps that in Marais' approach the removal is linked to the mass of active material generated per day (Siebritz *et al.* 1982). Until a satisfactory biochemically based model of P *release* and *uptake* is evolved it is unlikely that the full potential of processes, utilizing these phenomena for excess P *removal*, will be attained. Such a model to be successful should, in our opinion, provide answers to the behavioural pattern observed in P removal plants listed below:

(1) P release to the bulk liquid takes place under anaerobic conditions if readily biodegradable COD is present in the bulk liquid.*

(2) P uptake takes place if P release had been obtained and nitrate or oxygen is present.

(3) Release, uptake and excess removal are sensitively related to the concentration of readily biodegradable COD in the influent - addition of acetate or glucose to the influent is reflected in improved P removal performance.

(4) Anaerobic-aerobic sequencing appears to be essential in order to obtain P removal - in an anaerobic-aerobic plant that is removing P, if it is changed to operate as an aerobic-aerobic one, or, if sufficient nitrate is added to the influent of the anaerobic-aerobic plant so that nitrate is present in the anaerobic reactor, P removal immediately ceases. This indicates that, even though the appropriate organism may be present, specific conditions also must be present to obtain P removal.

(5) Anaerobic-aerobic conditions appear to promote the growth of P accumulating organisms. This aspect is particularly intriguing for many of the organisms implicated are obligate aerobes, for example *Acinetobacter*, yet these organisms apparently find considerable advantage for growth by passing through the anaerobic phase with substrate present (as indicated by their abundance in P removal plants, Buchan 1981). This behaviour is the more remarkable when it is noted that acetate promotes the growth of these organisms in the system even though this substrate is completely unavailable as an energy source to aerobes in the anaerobic zone, being one of the end products of the Embden-Meyerhof pathway.

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*Readily biodegradable COD implies, in a biochemical sense, a substrate that can readily pass through the cytoplasmic membrane of the cell by diffusion or osmotic pressure.

(6) From denitrification rate and oxygen utilization rate studies in the anoxic or aerobic reactors of a P removal process there is heavy competition for substrate between the polyP and other microorganisms whereas in the anaerobic reactor there can be competition only for substrates that can be utilized through anaerobic glycolysis e.g. the Embden-Meyerhof pathway.

Phosphate accumulation by organisms in P removal plants is but one instance of this phenomenon. Harold (1966) in an authoritative survey of the state of the art reports that polyphosphate accumulation is widespread among microorganisms and has been observed amongst others in bacteria, yeasts, fungi and phosynthetic algae. Phosphorus plays such a crucial role in biology that it must have been associated with life from the beginning. There is the suggestion that polyphosphates (polyP) and/or pyrophosphates predate adenosine triphosphates (ATP) as an energy carrier, that polyphosphate is a metabolic fossil which in time has lost its original function to assume new ones "which still elude us" (Harold 1966). From an evolution point of view if one considers the rapid adaptability and the frequency of mutation in microorganisms, any such new functions would have developed only if they accrued some advantage to the organism in its competitive struggle for survival otherwise their presence would have diminished with time. It seems therefore that if one could identify the function(s) of polyP accumulations it would go a long way to elucidating their biochemical behaviour.

With regard to function, Harold states that there is no clarity as to whether the polyP accumulations serve the function of phosphate storage or energy storage. He tended towards the phosphate storage hypothesis on the basis that the accumulation of polyP will suffice for several doublings of the cell mass should subsequent phosphate starvation occur and starvation of P is not unlikely, in nature generally P availability is low; also "polyP could constitute an accessible reserve for synthesis of messenger RNA, ribosomes and metabolic intermediates to facilitate the *initiation* of growth". Furthermore, he was of the opinion that storage of polyP "would minimize disturbance of the osmotic equilibrium and of the concentrations of the critical intermediates, Pi*, and andenine nucleotides."

Considering synthesis and degradation of polyP, Harold states that: "There appears to be only a single pathway for the biosynthesis of long-chain polyP. This is the reaction catalyzed by polyphosphate kinase, in which the terminal phosphoryl group of ATP is transferred to polyP according to the reaction (a) : $ATP + (Pi)_n \rightleftharpoons ADP + (Pi)_{n+1}$." With regard to the breakdown of polyP both polyphosphate kinase and Polyphosphotase are implicated. Polyphosphate kinase can act reversibly for both synthesis and degradation - there is evidence that some types of polyphosphate kinase may be involved in the transfer of phosphate from polyP to andenosine monophosphate (AMP) or for phosphorylation of glucose. Polyphosphotase, however, acts only in the degradation of polyP to phosphate.

The regulating mechanisms that control these reactions are but poorly understood. As an example of this lack of understanding, consider the mechanism that controls the accumulation of polyP in the so-called "polyphosphate overplus" phenomenon. This phenomenon is observed in organisms that can accumulate P when the organism is innoculated into a medium that contains all the substances necessary for growth i.e. salts and carbon energy, with the exception of a deficiency in *phosphate*. This deficiency causes that nucleic growth cannot occur but observations show that polyphosphate kinase and polyphosphotase increase in concentration. On addition of phosphate to the medium a rapid accumulation of polyP is catalyzed by the kinase, whereupon the kinase concentration commences to decrease but the phosphotase concentration remains high probably to break down the polyP to phosphate for nucleic acid synthesis. Regulation of these reactions poses the question: Is the increase in kinase during P deficiency regulated by the low concentration of P in the medium

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*Pi represents the phosphate radical; $(Pi)_n$ a polyP chain of n Pi units.

or by the ATP-ADP-P equilibrium within the organism? This same kind of question crops up where any other essential metabolite is absent, such as nitrogen or sulphur.

The behaviour patterns described above generally point to the hypothesis that P accumulation is a response to a stress condition in which the propensity for P accumulation confers an advantage on the organism in a way not evident.

The first endeavour to construct a biochemical model of P uptake and release in the activated sludge process is due to Osborn and Nicholls (1977) of Johannesburg City Council. Cognizant of the past work (as set out by Harold) they approached their subject from the standpoint that the polyP phenomenon is a response by the organism to the imposition of an *anaerobic stress*, that the polyP pools assist the organism in surviving the stressed state. This approach in itself constituted a bold extension on the work reported by the bacteriologists - they considered only aerobic systems, and the stresses they applied were by imposing deficiencies in selected metabolites.

In 1978 the Johannesburg group extended their work by proposing that "poly-β-hydroxybutyrate also plays an important rôle in maintaining the life cycle of aerobic and denitrifying organisms during their passage through the anaerobic zone", Hall, Nicholls and Osborn (1978). They state: "Under normal aerobic conditions sewage (as typified by glucose in the following equation) is oxidised in a series of steps to pyruvate, which results in the production of 4 hydrogen atoms and the liberation of 4 electrons

$C_6H_{12}O_6 \rightarrow 2CH_3\ CO\ COOH + 4H^+ + 4e^-$
Glucose pyruvic acid

These hydrogen ions and electrons are then passed through the Krebs (citric acid) cycle and finally meet up with oxygen from either the air or from nitrate, and are eliminated from the system as water.

"Under anaerobic conditions aerobic bacteria can metabolise substrate up to the formation of acetyl coenzyme A, and will die at this point if no alternative route is available to relieve the system of the accumulated hydrogen ions and associated electrons. Some bacteria have the ability to absorb these hydrogen ions and convert them into water insoluble poly-β-hydroxybutyrate where they can be, as it were, temporarily stored until aerobic conditions are restored. The poly-β-hydroxybutyrate reverts back to acetyl coenzyme A which then passes the liberated hydrogen out of the system as water via the aerobic Krebs cycle.

"Energy requirements for obligate aerobes finding themselves in an anaerobic environment can be supplied as indicated in the following equation:

Acetyl CoA + ADP + Pi → ATP + acetic acid + CoAH

where the ATP formed is used to support life-sustaining reactions. The phosphorus requirements are probably preferentially supplied from the polyphosphate pool.

"Many aerobic bacteria have the ability to form poly-β-hydroxybutyrate and the concept of this compound acting as a balancing facility for hydrogen ions, or as an electron sink, as it is now more commonly called, is probably the basis of survival of many bacteria when exposed to temporary conditions of anaerobiasis."*

From the abstract above the Johannesburg group appears to advance two mechanisms for survival in the anaerobic zone: (i) energy for ATP formation derived from the break up of polyP chains to phosphate and (ii) creation of a balancing facility for hydrogen ions and electrons by the formation of PBH. Generally the orientation of the Johannesburg model is towards survival. Judged against the six observations on P

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*The authors have quoted the writers at length for the passage above neatly summarises their approach to this problem. Details of the biological pathways are to be found in their papers.

removal process behaviour the main aspect in which the model is not persuasive is that it does not explain satisfactorily the evident *advantage* the polyP organisms appear to have in processes having anaerobic zones as indicated by their proliferation in these processes. However, this imputed deficiency aside, the model showed its worth in practical terms immediately*: Noting the rôle of the intermediates in poly-β-hydroxybutyrate formation and further, that the retention time in the anaerobic reactor is too short to process the particulate COD input via the Embden-Meyerhof pathway to produce intermediates, the group proposed that the intermediates be augmented as follows: Subject the underflow from the primary settling tank to acid digestion and feed the supernatant to the P removal plant. They experimented by introducing the acid digester supernatant to the anaerobic, anoxic or aerobic zone and found that the most promising results were associated with addition to the anaerobic zone. This outflow from their model has provided a means whereby the P removal propensity can be extended to plants treating influents deficient in readily biodegradable influent COD and merits serious attention in future research. The behavioural pattern, with acid addition, also provides direct support for the readily biodegradable COD hypothesis of the Cape Town group.

Rensink (1981) reported on the work on excess P removal at the Technical University of Wageningen, Holland. Following on the work of Osborn and Nicholls they concurred that the presence of polyphosphates served as a survival mechanism for polyP organisms during the anaerobic phase, but went further by hypothesizing that during the anaerobic phase the lower fatty acids present in the liquid phase are stored as PHB, the energy for formation of PHB being obtained by conversion of polyP to $PO_4^{\overline{3}}$ via ATP and ADP. In the aerobic zone the stored PHB is utilized for the dissimulation and assimulation functions of the organism, i.e., the PHB accumulated during the anaerobic phase provides a source of energy for growth of the polyP organisms in the aerobic zone over and above that available in competition with other non-polyP organisms in that zone. The storage mechanism indeed is of crucial importance; Rensink notes that *Acinetobacter*, for example, is a relatively slow growing organism so that in the aerobic zone, in the absence of the storage mechanism, this organism will show relatively minor growth in competition with other faster growing facultative organisms. The storage mechanism therefore explains the growth of polyP organisms in anaerobic-aerobic systems. Also, in terms of this hypothesis the mass of polyP organisms should be strongly linked to the mass of lower fatty acids available to this organism in the anaerobic zone.

Rensink demonstrated the conversion of the lower fatty acids to a higher energy form in the anaerobic reactor as follows: To an anaerobic sample of mixed liquor, from a P removing plant, acetate was added and monitored with time. In both filtered and unfiltered samples taken from the batch, the acetate concentration diminished with time and concomitantly the phosphate concentration in the filtered liquid increased. Disappearance of acetate from the filtered sample indicates absorbtion of the acetate by the organisms; disappearance from the unfiltered sample indicates transformation of the acetate to some other organic material, see Fig.10. To show that the acetate removal and P release and uptake are associated with the polyP organisms, a 10 in-series reactor system was operated, initially all aerobic, and it was found that P removal was that expected for normal metabolic requirements. On changing to an anaerobic/aerobic system (5 anaerobic, 5 aerobic), initially no P was released and uptake was normal, but gradually over a six-week period, release and excess uptake developed in an increasing degree. Over the same period the plant was periodically given a dose of acetate in the influent; at the start of the six-week period little or no acetate disappeared in the anaerobic reactor series but by the end of six weeks the acetate disappeared, to zero, by the third anaerobic reactor, see Fig. 11. Over the six-week period the polyP organisms also were found to increase indicating a correlation between the polyP organism growth and acetate disappearance. These results are very revealing and constitute a significant contribution towards elucidating the phenomenon of P uptake and release.

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*and justifies the effort in constructing such models.

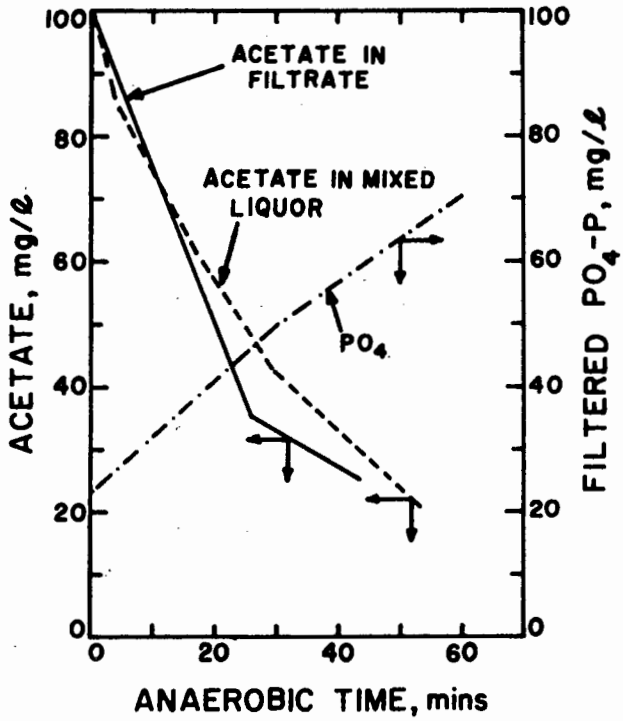

Fig.10. Change of acetate and increase in PO_4^- with time in an unaerated batch of mixed liquor from an excess P removal plant (After Rensink, 1981).

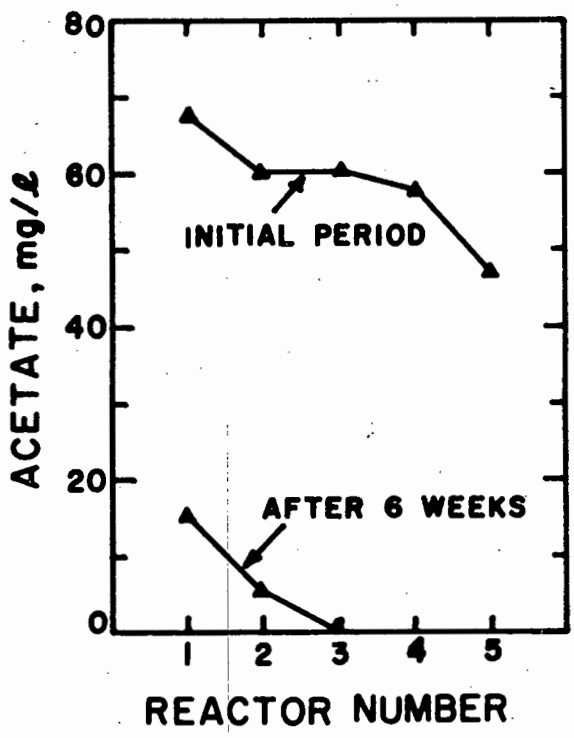

Fig.11. Acetate behaviour in the anaerobic zone, immediately after a change-over from a totally aerobic system to an anoxic-aerobic one, and after six weeks (After Rensink, 1982).

Rensink ascribes the presence of the lower fatty acids to the redox state in the anaerobic reactor - the lower this state the more the growth of facultative anaerobes will be promoted in the system, the greater the production of lower fatty acids and logically the higher the P removal. In this regard Rensink follows the same line of thought as Fuhs and Chen and Shapiro, that the fatty acids are produced in the anaerobic state at low redox potentials. This approach would appear to be in direct contrast to that proposed by the University of Cape Town group which proposes that the substrate that promotes excess release and uptake *is present in the influent* (the so-called rapidly biodegradable COD), and that the redox potential is not a significant parameter. A brief discussion on these two points of view will assist in clarifying the situation:

> Generally all substrates, except the lower fatty acids, must pass through the Embden-Meyerhof or some other equivalent pathway to convert the substrate to a form (for example, acetate or formate) suitable for entry into either the aerobic Krebs cycle or anaerobic fermentation pathway. It is important to note that this step is essential in both aerobic and anaerobic processes. The conversion rate is dependent on the type of substrate; Dold *et al.* (1980) has shown that in aerobic processes the utilization rate of particulate organic material is slow, whereas for some soluble substrates the rate is extremely rapid, approximately 7 to 10 times faster than for the particulate substrate. With the particulate substrate the rate limiting step appears to be the solubilization of the particulate matter whereupon it can pass into the

organism for energy production and fatty acid formation via the Embden-Meyerhof pathway. Similarly Eastman and Ferguson (1981) have shown that in anaerobic processes the rate limiting step for particulate substrate also lies in the solubilization of particulate organic material prior to lower fatty acids production. In both aerobic and anaerobic processes soluble substrates like glucose pass readily through the cytoplasmic membrane and are rapidly utilized for energy production, and for production of lower fatty acids via the Embden-Meyerhof pathway. As this pathway is operative in both aerobic processes, with high redox potential, and anaerobic processes, with low redox potential, it must be concluded that the Embden-Meyerhof reactions at best are only weakly affected by the redox potential.

From the discussion above there is good reason to believe that the production of lower fatty acids in the anaerobic reactor of P removal plants, under the usual modes of operation, will be minimal for particulate COD and probably is derived almost exclusively from the rapidly biodegradable COD.* It would be instructive therefore to enquire more closely into the fate of the rapidly biodegradable substrates *and* their interaction with the polyP organisms.

Interaction of the polyP organisms with the substrate cannot be done effectively unless a model of polyP behaviour is hypothesized. Then if it can be shown in biochemical terms that the model is consistent, this would provide a basis for experimental investigation to test the model. A model for the polyP organism behaviour can be constructed if the following hypothesis is accepted:

> *PolyP accumulation serves as an energy reservoir, to sustain the organism during the anaerobic stressed state, but principally to gain a positive advantage over non-P accumulating organisms by partitioning of readily biodegradable COD (in the lower fatty acid form) in the anaerobic state for its exclusive use subsequently in the aerobic state.*

The biochemical behaviour is envisaged as follows:

In the formation of a polyP chain the linking of two phosphate radicals requires the input of about 1 ATP (7 kcal/mole P). When this bond is broken the same quantity of energy is released for work, and a phosphate radical is released. Under anaerobic conditions with readily biodegradable COD surrounding the organisms, when polyP is degraded it provides P and energy to form ATP. The ATP is used to bring substrate into the cell and to convert the substrate to a lipid form available for storage as aceto-acetate and/or poly-β-hydroxybutyrate. Two types of substrates are to be considered, first, a relatively 'low energy' short chain fatty acid which cannot yield biological energy through anaerobic glycolyses, e.g. acetate, and second, a relatively 'high energy' substrate which can be used by facultative and aerobic organisms to yield energy through anaerobic glycolysis, e.g. glucose.

Acetate: Acetate entering the cell will be complexed by the enzyme CoA to form acetyl CoA, a reaction requiring an input of energy of 2 ATP. This is achieved as follows: An ATP is formed from ADP + Pi + 7 kcal/mole P where Pi and the energy is produced by breaking of a phosphate radical (Pi) from the polyP chain $(Pi)_n$ which yields 7 kcal/mole P., i.e.

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*Under high anaerobic mass fractions and low recycles giving rise to long actual anaerobic retention times, acid formation from the slowly biodegradable COD fraction may become of significance and probably is contributory to excess P removal for example in the process of Kerdachi and Roberts (1982); however, their mode of operation results in a process behaviour that is (i) oxygen limited rather than the normally COD limited state, and (ii) the anaerobic mass fraction is so large, 80 to 90 percent, that the metabolic processes appear to deviate significantly from that normally observed, for example, the sludge produced per day in their plant appears to be 75 to 100 percent more than that normally expected.

$$2ADP + (Pi)_2 = 2ATP \quad (1)$$

$$\text{acetate} + 2ATP + \text{Co-A} \rightarrow \text{acetyl CoA} + 2ADP + 2Pi \quad (2)$$

This step would in fact reduce the acetate concentration within the organism allowing an osmotic pressure to be created for further entry of the substrate. The organism has only a limited supply of Co-A so that acetyl Co-A will not be a convenient means of storing the ingested substrate. Storage is more likely as a lipid of the form acetoacetate (or perhaps hydroxybutyrate, see below), i.e.

$$2 \text{ acetyl Co-A} + 2ADP + 2Pi \rightarrow \text{acetoacetate} + 2ATP + 2\text{Co-A} \quad (3)$$

The overall energy required in the storage of acetate as acetoacetate is given by 2 times Eq (2) plus Eq (3) i.e.

$$2 \text{ acetate} + 2ATP \rightarrow \text{acetoacetate} + 2ADP + 2Pi \quad (4)$$

Thus, to store a molecule of acetoacetate (originally from 2 molecules of acetate) requires that 2Pi are *released*, these originating from the polyphosphate store, thereby increasing P continuously in the cell, creating an osmotic pressure of P which diffuses through the cytoplasmic membrane and increases the P concentration in the bulk liquid.

Glucose: Where glucose is the readily available substrate two situations may arise, (a) the polyP organisms may not be able to utilize glucose (or any other simple sugar) as the carbon source - according to Fuhs and Chen (1975) this is the case with regard to *Acinetobacter*; or (b), polyP forming organisms can utilize glucose as a substrate.

(a) PolyP organisms cannot utilize glucose:

For this situation in a mixed culture the facultative organisms only will utilize glucose as an anaerobic energy source via the Embden-Meyerhof pathway, the two principal steps being

(i) Glucose to pyruvate:

$$1 \text{ Glucose} + 2ADP + 2NAD_{OX} \rightarrow 2 \text{ Pyruvate} + 2ATP + 1NAD_{RED} \quad (5a)^*$$

(ii) Pyruvate to short chain fatty acids:

The reaction is depicted as follows:

$$2 \text{ Pyruvate} + 2NAD_{RED} \rightarrow 3 \text{ Acetate} + 2NAD_{OX} \quad (5b)$$

In this step pyruvate is reduced (i.e. accepts the electrons from NAD_{RED}) to form the by-product of fermentation - acetate, and NAD_{OX} is regenerated. The overall reaction, for (i) and (ii) above, for the Embden-Meyerhof breakdown of glucose, is given by the sum of reactions (5a and 5b) above, i.e.

$$1 \text{ Glucose} + 2ADP + P \rightarrow 3 \text{ Acetate} + 2ATP \quad (6)$$

(Note that P in Eq (6) does not originate from polyP but from P present in the cytoplasm).

At the completion of reaction (6), the facultative organism is in the same electron state as before the reaction, except that it is at a higher energy level, by 2ATP/molecule of glucose; the bulk concentration of acetate has also increased by three molecules. The acetate cannot be utilized further by the facultative organisms while in an anaerobic state. If polyP organisms are present in the mixed culture, the acetate is available for storage as acetoacetate, as set out under acetate utilization above. Consequently, by being

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*NAD (nicotinamide adenine dinucleotide) is an electron carrier in the cell, the reduced and oxidized states being depicted as NAD_{RED} and NAD_{OX} respectively. The ratios of NAD_{OX}/NAD_{RED} and ADP/ATP both serve as regulating parameters in feed-back mechanisms controlling many of the transformation reactions in which they are involved.

in a mixed culture in the anaerobic state the polyP organism receives substantial benefit by being able to utilize the products of the glycolysis reaction (by the facultative organisms) of an input substrate it cannot use directly. If glucose was fed to a pure culture of polyP organisms (of the polyP strain under discussion) the mechanisms set out above would not be possible.

(b) PolyP organisms can accept glucose as a carbon source:

In this situation *both* the facultative and polyP organisms will compete for the glucose molecules surrounding them. For both species the glucose will be broken down in the Embden-Meyerhof pathway according to reaction (5a) above. Thereafter the action of the two groups of organisms may differ. The facultative organism continues via reactions (5b and 6) to discharge acetate. In some strains of polyP organisms there may exist a pathway whereby utilizing the electrons (as NAD_{RED}) and pyruvate generated in reaction (5a), the pyruvate is transformed to poly-β-hydroxybutyrate (PHB) which can be stored in these organisms. The storage mechanism can be depicted as follows:

(i) The pyruvate is oxidized to acetyl Co-A with NAD_{OX} acting as the electron acceptor:

$$2 \text{ Pyruvate} + 2NAD_{OX} + 2 \text{ Co-A} \rightarrow 2 \text{ Acetyl Co-A} + 2 \ CO_2 + 2NAD_{RED} \quad (7)$$

(ii) Acetyl Co-A is converted to acetoacetate:

$$2 \text{ Acetyl Co-A} \rightarrow \text{acetoacetate} + 2 \text{ Co-A} \quad (8)$$

(iii) Acetoacetate acts as electron acceptor to form β-hydroxybutyrate:

$$\text{Acetoacetate} + 1NAD_{RED} \rightarrow 1 \ \beta\text{-hydroxybutyrate} + 1NAD_{OX} \quad (9)$$

The overall reaction is formulated by adding reactions (5a, 7, 8 and 9), i.e.

$$1 \text{ Glucose} + 3NAD_{OX} + 2ADP + 2P \rightarrow 1\beta\text{-hydroxybutyrate} + 2 \ CO_2 + 2ATP + 3NAD_{RED} \quad (10)$$

The overall reaction indicates that 2ATP and $3NAD_{RED}$ are produced from 1 Glucose. Unless the organism can find a sink for the $3NAD_{RED}$ the organism would not be viable. From this it would appear that the pathway above is unlikely in a pure culture of this organism. However, in a mixed culture the facultative organisms (in competition for the glucose) would discharge acetate but the polyP organisms utilizing its polyP store to generate ATP (according to reaction (1)) can use the excess NAD_{RED} in reaction (10) to transform the acetate to acetoacetate and then to PHB in accordance with reactions (2 and 3), and reaction (9) respectively. The proportions of the relative mass fractions of acetoacetate and PHB stored probably will be controlled by the relative fractions of facultative and polyP organisms and the mass and type of substrate available. Here again, it is apparent that a mixed culture while in the anaerobic state confers an advantage on the polyP organisms in that the mixed nature of the culture promotes the sequestering of the readily available substrate for the subsequent exclusive use by the polyP organisms.

PolyP formation and P_i storage: When the polyP organism with its stored substrate enters an aerobic (or anoxic) region, the stored substrate will be oxidized immediately giving rise to a rapid increase in the ATP/ADP ratio which in turn will act as a feed-back mechanism activating (or producing) polyP kinase to catalyze polyP production in order to refill the polyP pool. (The same type of control probably also acts under anaerobic conditions: the ATP/ADP ratio will decrease acting as a feed-back mechanism activating (or producing) polyphosphotase to catalize the breakdown of stored polyP to P_i for ATP production).

Energy considerations: To illustrate the advantage accruing to the polyP organism by its sequestering action, acetate will be used as an example. From reaction (4) it is shown that 2ATP (from the polyP pool) is required for two molecules of acetate to be converted to the storage form of acetoacetate. Under aerobic conditions, through the Kreb cycle and subsequent oxidative phosphorylation, the overall

reaction is

$$1\ \text{Acetoacetate} + 4\ O_2 + 8NAD_{RED} + 22ADP + 22P \rightarrow 4CO_2 + 8H_2O + 8NAD_{OX} + 22ATP \quad (11)$$

Now two acetates are needed to form one acetoacetate, consequently, from reaction (11) for each acetate stored in the cell 11ATP will become available under aerobic conditions. To store this acetate requires 1ATP. Hence, from an investment of 1ATP from its polyP pool, 11ATP is returned. This would not have been possible if the organism did not have the polyP storage propensity.

The analysis above was restricted to two substrates, acetate and glucose, to illustrate the different pathways required by the polyP organism to utilize these. In the real world, the substrate will consist probably of many types but the mechanisms described above very likely will still apply.

The bioenergetics model described above would appear to explain the six behavioural patterns observed on large plants listed at the beginning of this section. Also, it supports the proposal from the Johannesburg group that addition of acid digestion supernatant would have a significant effect on P release, uptake and excess removal, even though the last two have not been dealt with in depth in the model presented. Having an hypothesized model should facilitate development of experimental designs to test its validity, and more important, to optimize P removal in full scale plants.

CONCLUSION

This paper has traced the development of the concept of biological excess phosphorus removal in activated sludge from its first reported manifestation in 1959 to the present. The cumulative evidence towards its existence is persuasive and there should not remain much doubt that the phenomenon is biological. Its theoretical description, in a biochemical or bioenergetic sense however, is still in a rudimentary stage. The parametric black box approach in its development and application to design and optimization of P removal plants, which up to now has dominated enquiry, probably has past the peak of its usefulness as a research tool. The direction of future research is likely to be influenced increasingly by the biochemical aspects of the phenomena; any significant advances in the use of this phenomenon in waste water treatment will, in the opinion of the authors, be contingent on greater understanding of the biochemical mechanisms controlling the phenomenon.

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REFERENCES

Alarcon, G.O. (1961). Removal of phosphorus from sewage. Masters essay, John Hopkins Univ., Baltimore Md.

Buchan, L. (1981). The location and nature of accumulated phosphorus in seven sludges from activated sludge plants which exhibited enhanced phosphorus removal. Water S.A., 7, 1-7.

Barnard, J.L. (1975). Biological nutrient removal without the addition of chemicals. Water Research, 9, 485-490.

Barnard, J.L. (1975). Nutrient removal in biological systems. Wat.Pollut. Control, 74, 2, 143-154.

Barnard, J.L. (1976). A review of biological phosphorus removal in the activated sludge process. Water S.A., 2, 3, 136-144.

Davelaar, D., T.R.Davies and S.G.Wiechers (1978). The significance of an anaerobic zone for biological removal of phosphate from wastewaters, Water S.A., 4, 2, 54-60.

Dold, P.L., G.A.Ekama and G.v.R.Marais (1980). A general model for the activated sludge process. Prog.Wat.Tech., 12, 47-77.

Eastman, J.A. and J.F.Ferguson (1981). Solubilization of particulate organic carbon during the acid phase of anaerobic digestion. W.P.C.F., 53, 3, 352-366.

Ekama, G.A., I.P.Siebritz and G.v.R.Marais (1982). Considerations in the process design of nutrient removal activated sludge processes. Presented at the I.A.W.P.R. post-conf. seminar on Phosphate removal, Pretoria, April 1982.

Ekama, G.A., A.C.van Haandel and G.v.R.Marais (1979). The present status of research on nitrogen removal : a model for the modified activated sludge process. Presented at the Symposium on Nutrient Removal, S.A. Branch of I.W.P.C. Pretoria, May 1979. Proceedings published by Water Research Commission of South Africa.

Fuhs, G.W. and M.Chen (1975). Microbiological basis of phosphate removal in the activated sludge process for the treatment of wastewater. Microbial Ecology, 2, 119-138.

Hall, E., H.A.Nicholls and D.W.Osborn (1978). Progress in Johannesburg towards the biological removal of phosphorus from sewage effluents. Presented at 11th Essen Conference, Institute of Water Quality and Water Quality Management.

Harold, F.M. (1966). Inorganic polyphosphates in biology : structure, metabolism and function, American Society of Microbiology - Bacteriological reviews, 30, 772-794.

Hoffmann, R. and G.v.R.Marais (1977). Phosphorus removal in the modified activated sludge process. Research Report W 22, Dept. of Civil Eng., Univ. of Cape Town.

Kerdachi, D.A. and M.R.Roberts (1982). Full scale phosphate removal experiences in the Umlatuzana works at different sludge ages. Presented at the I.A.W.P.R. post-conference seminar on Phosphate removal in biological treatment processes, Pretoria. Proc. to be published in Water Science and Technology.

Lawson, E.N. and N.E.Tonhazy (1980). Changes in morphology and phosphate uptake patterns of *Acinetobacter calcoaceticus strains*, Water S.A., 6, 3, 105-112.

Levin, G.V. and J.Shapiro (1965). Metabolic uptake of phosphorus by wastewater organisms. W.P.C.F., 37, 6, 800-821.

Marsden, M.G. and G.v.R. Marais (1977). The rôle of the primary anoxic reactor in denitrification and biological phosphorus removal. Research Report W 19, Dept. of Civil Eng., Univ. of Cape Town.

Martin, K.A.C. and G.v.R.Marais (1975). Kinetics of enhanced phosphorus removal in the activated sludge process. Research Report W 14, Dept. of Civil Eng., Univ. of Cape Town.

McLaren, A.R. and R.J.Wood (1976). Effective phosphorus removal from sewage by biological means. Water S.A., 2, 1, 47-50.

Milbury, W.F., D.McCauley and C.H.Hawthorne (1971). Operation of conventional activated sludge for maximum phosphorus removal. W.P.C.F., 43, 9, 1890-1901.

Nicholls, H.A. (1978). Kinetics of phosphorus transformations in aerobic and anaerobic environments. Presented at 9th I.A.W.P.R. post-conf. seminar, June 1978, Copenhagen. Prog.Wat.Tech., 10.

Nicholls, H.A., D.W.Osborn and G.v.R.Marais (1982). Performance of large scale nutrient removal activated sludge plants. Research Report W 43, Dept. of Civil Eng., Univ. of Cape Town.

Ohsumi, T., M.Shoda and S.Udaka (1980). Influence of cultural conditions on phosphate accumulation of *Arthrobacter globiformis* PAB-6, Agric. Biol. Chem., 44, 2, 325-331.

Osborn, D.W. and H.A.Nicholls (1977). Optimization of the activated sludge process for the biological removal of phosphorus, I.A.W.P.R. Conf. on Advanced Treatment and Reclamation of Wastewater. Johannesburg, 1977. Prog Wat.Tech., 10, 1/2, 261-277.

Rabinowitz, B. and G.v.R.Marais (1980). Chemical and biological phosphorus removal in the activated sludge process. Research Report W 32, Dept. of Civil Eng., Univ. of Cape Town.

Randall, C.W., D.W.Marshall and P.H.King (1970). Phosphate release in activated sludge process. J.San.Eng.Div., ASCE, 96, SA2, 395-408.

Rensink, J.H. (1981). Biologische defosfatering en procesbepalende faktoren. In, Symp.Boek - Defosfatering; nieuwe ontwikkelingen en praktijkervaringen in Nederland en Zweden. NVA Symp. (in Dutch).

Rensink, J.H., H.J.G.W.Donker and H.P.de Vries (1981). Biological P-removal in domestic wastewater by the activated sludge process. Presented at 5th European Sewage and Refuse Symposium, Munchen, June, 1981, Procs. 487-502.

Scalf, M.R., F.M.Pfeffer, L.D.Lively, J.O.Witherow and C.P.Priesing (1969). Phosphate removal at Baltimore, Maryland. J.San.Eng.Div., ASCE, 95, SA5, 817-827.

Sekikawa, Y., S.Nishikawa, M.Okazaki and K.Kato (1966). Release of soluble orthophosphate in activated sludge process. W.P.C.F., 38, 3, 364-365.

Shapiro, J. (1967). Induced rapid release and uptake of phosphate by microorganisms. Science, 155, 1269-1271.

Shapiro, J., G.V.Levin and H.Zea G. (1967). Anoxically induced release of phosphate in wastewater treatment. W.P.C.F., 39, 11, 1811-1818.

Shoda, M., T.Ohsumi and S.Udaka (1980). Screening for high phosphate accumulating bacteria, Agric.Biol.Chem., 44, 2, 319-324.

Siebritz, I.P., G.A.Ekama and G.v.R.Marais (1980). Excess Biological Phosphorus Removal in the Activated Sludge Process at Warm Temperate Climates. Proc. Waste Treatment and Utilization, Vol.2, 233-251, Eds. C.W. Robinson, M.Moo-Young and G.J.Farquhar, Pergamon Press, Toronto.

Siebritz, I.P., G.A.Ekama and G.v.R.Marais (1982). A parametric model for biological excess phosphorus removal. Presented at the I.A.W.P.R. post-conference seminar on phosphate removal, Pretoria. Procs. to be published in Water Science and Technology.

Simpkins, M.J. and A.R.McLaren (1978). Consistent biological phosphate and nitrate removal in an activated sludge plant, Prog.Wat.Tech., 10, 5/6, 433-442.

Srinath, E.G., C.A.Sastry and S.C.Pillai (1959). Rapid removal of phosphorus from sewage by acivated sludge. Water and Waste Treatment, 11, 410.

Stern, L.B. and G.v.R.Marais (1974). Sewage as the electron donor in biological denitrification. Research Report W 7, Dept. of Civil Eng., Univ. of Cape Town.

Vacker, D., C.H.Connell and W.N.Wells (1967). Phosphate removal through municipal wastewater treatment at San Antonio, Texas. W.P.C.F., 39, 5, 750-771.

van Haandel, A.C., P.L. Dold and G.v.R.Marais (1982). Optimization of Nitrogen removal in the single sludge activated sludge process. Presented at 11th I.A.W.P.R. Conf. Cape Town. To be published in Water, Science and Technology.

van Haandel, A.C., G.A.Ekama and G.v.R.Marais (1981). The activated sludge process Part 3 - single sludge denitrification. Water Research, 15, 1135-1152.

Wells, W.N. (1969). Differences in phosphate uptake rates exhibited by activated sludges. W.P.C.F., 41, 5, 765-771.

Witherow, J.L. (1970). Phosphate removal by activated sludge. Proc. 24th Ind. Waste Conf., Purdue Univ., Ext. Ser. 135, 1169-1184.

Yall, I., W.H.Boughton, R.C.Knudsen and N.A.Sinclair (1970). Biological uptake of phosphorus by activated sludge. Applied Microbiology, 20, 1, 145-150.

Wat.Sci.Tech., 15, 3/4, 127-152, 1983

A PARAMETRIC MODEL FOR BIOLOGICAL EXCESS PHOSPHORUS REMOVAL

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Abstract

Biological excess phosphorus removal in nitrification-denitrification single sludge activated sludge processes is shown to be stimulated by having a concentration of rapidly biodegradable COD (S_{bsa}) $\geq$25 mg/ℓ in the anaerobic reactor; the magnitude of the P removal is determined by a P removal propensity factor (P_f) defined by the product of (S_{bsa}-25) and the fractional mass of sludge in the anaerobic reactor. S_{bsa} is rapidly depleted by nitrate entering the anaerobic reactor; in the Phoredox process treating municipal waste flows if the TKN/COD ratio of the influent is greater than about 0,08 mgN/mgCOD the process, if designed to ensure efficient nitrification, is unlikely to remove all the nitrate and nitrate is recycled to the anaerobic reactor whereupon P removal declines. A new process is proposed that protects the anaerobic reactor from the nitrate in the effluent; tests indicate that this process can give excess P removal for TKN/COD ratios up to 0,14 mgN/mgCOD.

INTRODUCTION

One of the main difficulties in devising an activated sludge process to give excess biological phosphorus (P) removal has been the lack of an acceptable mechanistic explanation of the phenomenon. Although a number of mechanisms have been advanced, process configurations and operational procedures to exploit such mechanisms have not, as yet, supported the hypothesized mechanisms unambiguously; evidently some aspects that affect the phenomena are not yet identified or correctly understood. Research into the process *per se* has, as a consequence, been forced to take the approach: "Let us see what happens if .....". The body of information that has been built up by this approach, although of a parametric or heuristic nature, has attained its own momentum and, in turn, provides data and situations which may be exploited by investigators focussing on the mechanistic aspects.

Since 1970 the University of Cape Town group has been engaged in intensive research into the activated sludge process. From the times Barnard in 1973 and 1975 proposed the respective explicit process configurations to remove nitrate and phosphorus biologically in the single sludge process, the group included enquiry also into these two phenomena as part of its research program. In this regard the group accepted, as a basic proposition, that nitrate and excess P removal are biologically mediated phenomena and hence should be viewed as integral parts of the general theory of the activated sludge process. In time this policy has proved to be a sound one

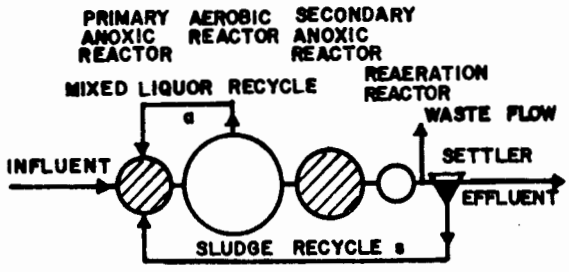

Fig.1. The Bardenpho process for biological nitrogen removal.

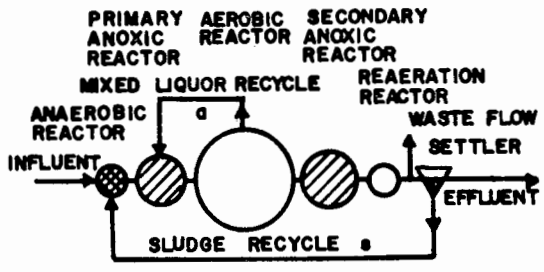

Fig.2. The Phoredox process for biological nitrogen and phosphorus removal.

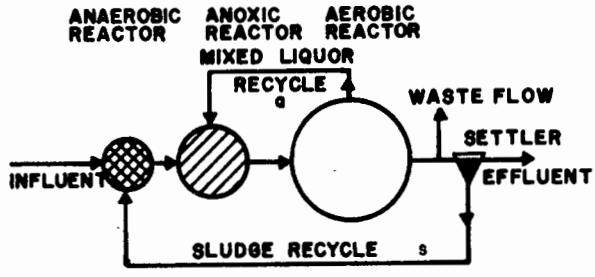

Fig.3. The modified Phoredox process for biological nitrogen and phosphorus removal.

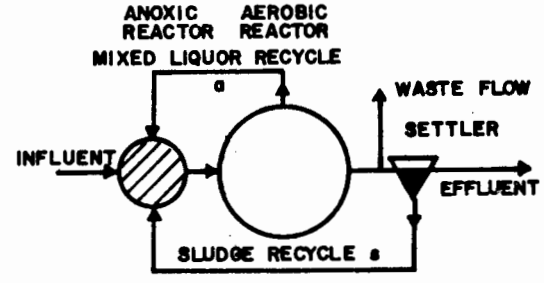

Fig.4. The modified Ludzack-Ettinger process for biological nitrogen removal.

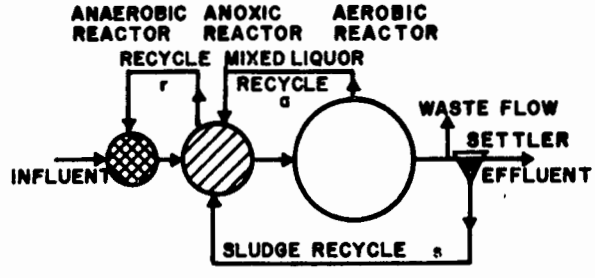

Fig.5. The UCT process for biological nitrogen and phosphorus removal.

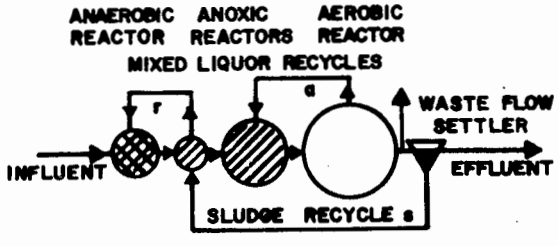

Fig.6. The modified UCT process for biological nitrogen and phosphorus removal.

because research into denitrification contributed considerably to the understanding of the aerobic process kinetics, and it was only after the establishment of the general nitrification-denitrification activated sludge model that it has become possible to make headway towards *describing* biological excess phosphorus removal even though the phenomenon is not yet *understood*.

In this paper the development of a quantitative semi-empirical parametric method for describing excess phosphorus removal will be briefly set out. A semi-historical approach is adopted as this will contribute to an overall appreciation of both the problem and the difficulties attendant in finding a solution.

EARLIER DEVELOPMENTS

With regard to excess P removal, from the reports of earlier investigators (e.g. Fuhs and Min Chen 1975, Barnard 1976) one conclusion has emerged which now appears to be generally accepted, i.e. excess removal is stimulated by stressing the organism by withholding the oxygen supply. Quantification of this stress, however, has presented major obstacles principally for two reasons, (1) the parameter in terms of which the stress is to be formulated is unknown and (2) in nitrification-denitrification systems introduction to and the presence of nitrate in the unaerated reactors are confounding factors that have complicated the problem of identification of the stress parameter. These difficulties will be evident in much of the presentation that follows.

Barnard (1974) in pilot scale studies on the Bardenpho process (Fig.1) reported that excess biological P removal is induced if at some point in the process configuration the organism mass is stressed by subjecting it to an "anaerobic" state (i.e. a state in which neither oxygen nor nitrate is present) such that phosphorus is released by the sludge mass to the bulk liquid. He proposed to produce this state efficiently by including an anaerobic reactor ahead of the primary anoxic (or pre-denitrification, pre-D) reactor in the Bardenpho process, this reactor receiving the influent flow and the underflow recycle from the secondary settling tanks, (Fig.2). This configuration has become known as the 5-stage Phoredox or simply as the Phoredox system.

For design purposes the criterion for P release did not prove helpful because it gave no guidance as to when the release could be expected. Barnard (1976) proposed that the anaerobic reactor be given a nominal retention time (mean daily flow/anaerobic volume) of one hour presumably because, from his pilot scale studies, this retention time gave rise to P release and adequate P removals.

To explain the excess removal phenomenon, Barnard in 1976 hypothesized that it is not the release *per se* that stimulates the excess uptake mechanism but that the release indicates that a certain low redox potential has been established, i.e. that the low redox potential triggers off the release and thereby stimulates excess P uptake. In terms of this hypothesis nitrate recycled via the underflow to the anaerobic reactor will restrain, in some degree, the level to which the redox potential can be lowered and consequently, nitrate can be expected to influence excess P uptake adversely. However, apparently he accepted that the Phoredox process can always be designed to denitrify completely in which event the recycle will contain zero nitrate, and the redox potential in consequence will attain the required low value. No measurements of the redox potential were reported.

Nicholls (1975) at full scale, and McLaren and Wood (1976) and Simpkins and McLaren (1978) at laboratory and pilot scale applied the Phoredox process at approximately 20°C to treat effluents from Johannesburg and Pretoria, and were successful in attaining excess P removal. They were also successful in obtaining excess removal in the Modified or 3-stage Phoredox (Fig.3) i.e. a Phoredox process without the post-denitrification (post-D) and reaeration reactors. Simpkins and McLaren found that (1) the anaerobic reactor was necessary for excess P removal, (2) nitrate in the recycle adversely affected P removal and (3) increasing the volume of the anaerobic reactor increased the excess P removal. These findings were in conformity with Barnard's redox potential hypothesis although again no redox potential measurements were taken.

None of the investigations above provided a reliable model to predict the magnitude of the denitrification to be expected even though it was evident from their experimental work that for design, evaluation of the nitrate in the recycle would appear to be crucial in assessing the success of a process both in stimulation of the P release and magnitude of the P uptake.

Marais and his group (Stern 1974, Martin 1975, Marsden 1976, Wilson 1976, with Marais) recognized the importance of quantitization of nitrate removal. In the Bardenpho process they replaced the completely mixed pre- and post-D reactors by plug flow reactors and, by measuring the nitrate along the reactor axes under constant flow and load conditions, investigated the kinetics of denitrification. They found that:

(1) In the pre-D reactor nitrate reduction took place in two consecutive linear phases; in the post-D reactor in a single linear phase. They formulated the system reduction* of nitrate concentration, ΔN, as follows:

*System reduction - reduction in concentration relative to the influent flow; actual reduction - reduction in actual concentration between influent and effluent of a reactor. Suppose actual reduction, ΔN_a, takes place in a reactor with recycle with respect to base flow of r and base flow Q, the system reduction, ΔN, is given by $\Delta N.Q = N_a.Q.(r+1)$.

$$\Delta N = K_1 X_a t + K_2 X_a (R_1 - t) + K_3 X_a R_3$$

(2) The reaction defined by K_1 persisted only for 1 to 10 minutes (i.e. $1<t<10$ minutes) so that normally the reaction was complete well within the retention time R_1 (2-3 hours) of the plug flow reactor; also, the reduction due to the K_1 reaction was approximately proportional to the biodegradable influent COD, S_{bi}, and the system removal could be expressed adequately by

$$\Delta N = \alpha S_{bi} + K_2 X_a R_1 + K_3 X_a R_3 \qquad (1)$$

where

R_1, R_3 = nominal retention time (h)

K_1, K_2, K_3 = denitrification rates ($mgNO_3$-N/mgX_a/h)

$K_1 = 0{,}03(1{,}20)^{(T-20)}$ for $T > 14°C$

$K_2 = 0{,}0042(1{,}08)^{(T-20)}$ for $T > 14°C$

$= K_3$ for $T < 14°C$

$K_3 = 0{,}0032(1{,}03)^{(T-20)}$ for $10°C<T<25°C$

X_a = active mass concentration (mgVASS/ℓ)

Δ_N = $mgNO_3$-N removed/ℓ of influent flow

S_{bi} = biodegradable influent COD concentration

α = 0,028 $mgNO_3$-N/mg biodegradable COD

t = duration time of K_1 reaction (h)

(3) Equation (1) was found to apply provided the nitrate was not reduced to zero in one or both of the anoxic reactors. If, in a particular reactor, nitrate was reduced to zero then by increasing the nitrate input to the reactor, (by increasing the recycle for example), the system nitrate removal increased, the zero nitrate point moved along the reactor axis towards the effluent end, until nitrate appeared in the effluent. Once this happened any further increase in the recycle had no effect on the system nitrate removal.

(4) The removal of nitrate could be increased by increasing the volumes of the anoxic reactors at the expense of the aerobic reactor volumes, i.e. increasing the unaerated sludge mass fraction of the system, but this fraction could not be increased *ad lib;* if increased above some critical value nitrification ceased. The upper limit was found to be a function of the maximum specific growth rate of the nitrifiers at the process temperature, μ_{nmT}, and the sludge age, R_s. It was further observed that μ_{nmT} appeared to differ for every waste flow investigated. The μ_{nmT} was not measured directly but the relative magnitude of μ_{nmT} was evident by noting the maximum unaerated mass fraction that could be tolerated before nitrification ceased. For example with one waste flow, nitrification ceased at an unaerated mass fraction of 0,3 (at 14°C and R_s=20 days), whereas for another this occurred only at an unaerated mass fraction of 0,55.

(5) To ensure that efficient nitrification takes place (>95 percent conversion of available TKN) it was necessary to increase the aerobic mass fraction to a value greater than the minimum that just allows nitrification; an increase of 25 percent (S_f=1,25) in the aerobic sludge mass fraction calculated at the lowest process temperature expected will guarantee efficient nitrification throughout the temperature range even under cyclic flow conditions.

The denitrification formulation, Eq.(1), although without any rational link to the activated sludge theory was found to provide a close description of nitrate removal in the Bardenpho process under constant flow and load conditions. The restriction on the unaerated mass fraction, (4) and (5) above, to satisfy the requirement of efficient nitrification, may result in insufficient anoxic sludge mass to guarantee

total nitrate removal. When total nitrate removal is not possible then, because $K_1 > K_3$ (for T >14°C) a consequence of Eq.(1) is that for maximum removal the post-D reactor should be omitted and its volume added to the pre-D reactor - to give the modified Ludzack-Ettinger (MLE) configuration, Fig.4. Under these conditions the MLE configuration will produce a lower nitrate effluent than the equivalent Bardenpho.

As part of the investigation into denitrification using the Bardenpho and MLE processes, measurements on P release in the pre- and post-D reactors, and excess uptake were taken. These results indicated that:

(1) A pre-D reactor, irrespective of whether it is in an "anoxic" or "anaerobic" state*, always stimulated some excess P removal whereas a post-D reactor appeared to have virtually no effect.

(2) Over periods of time excellent excess P removal was obtained with nitrate *present* in the pre-D reactor, in which event the removal took place principally in the pre-D reactor. Over other periods P release was observed in the pre-D reactor *with nitrate present* in which event the excess uptake took place in the aerobic reactor.

(3) Using the MLE process with anoxic mass fractions ranging from 0,07 to 0,33, under a constant a-recycle of 2, to give actual anoxic retention times, (volume of reactor/actual flow),ranging from 15 to 90 minutes, maximum excess P removal was attained at an actual anoxic retention time of about 30 minutes (anoxic mass fraction = 0,13) when the nitrate in the *effluent* from the anoxic reactor was 14 mg/ℓ! Excess system removal achieved was 8,2 mgP/ℓ for an influent COD of 660 mg/ℓ. When the anoxic mass fractions were increased above or decreased below this optimal value the excess removal decreased concomitantly.

The phosphorus removal response observed above is difficult to reconcile with the observations of Barnard, Nicholls, Simpkins and others reported earlier - all these investigators found that P release under anaerobic conditions was a prerequisite to excess uptake. Perhaps a different mechanism operated which has not yet been identified.

The approach described above eventually was abandoned because (1) the process response appeared to be rather unpredictable and, more important, (2) the small anoxic mass fractions apparently necessary to achieve high excess removal resulted in relatively inefficient nitrate removal. Because of the second reason principally the UCT group turned their attention to the P removal characteristics of the Phoredox process, (Rabinowitz and Marais, 1980).

The basic configuration selected was the 3-stage Phoredox; it was selected in preference to the 5-stage for the following reason: The sewage source did not allow an unaerated mass reaction of greater than 40 percent at 14°C for a sludge age (R_S) of 20 days if efficient nitrification was to be maintained; taking account of the fact that in the Phoredox process the anaerobic reactor cannot contribute its full denitrification potential for measured TKN/COD ratio of this waste flow, the 5-stage process could not reduce the nitrate to zero. Consequently, as discussed earlier, the post-D reactor volume was added to the pre-D to obtain the maximum nitrate re-

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*Anoxic; anaerobic: The meaning we will attach to these two terms, in nitrification-denitrification processes, follows that originally used by Barnard, i.e. Anoxic: a state in which nitrate is present but no oxygen; Anaerobic: a state in which neither nitrate nor oxygen is present. The inadequacies of these definitions is apparent when attempting to compare the state of two reactors of the same size in a completely mixed and a plug flow reactor respectively. A completely mixed anaerobic reactor, for example, will have no nitrate in the reactor and effluent; the equivalent plug flow reactor however may contain nitrate for a considerable portion of the reactor length i.e. be partly "anoxic", partly "anaerobic" - the inadequacy arises in that no indication is given as to the *intensity* of the state.

moval and hence the minimum nitrate in the underflow recycle. The findings from this investigation can be summarized as follows:

(1) When the nitrate concentration in the effluent (and underflow recycle) was low usually P release and excess uptake were observed. In general there was a tendency for the excess uptake to decrease quite disproportionately as the nitrate in the recycle increased, a behaviour also noted by Simpkins and McLaren and Barnard.

(2) With different batches of sewage having the *same* nitrate concentration in the recycle, one batch may give high P release and excess removal whereas the next may give no (or little) release and little excess removal. No apparent reason for this behaviour could be discovered.

The overall P removal performance was disappointing; not only did the plant not remove P in excess over long periods of time but the removal was erratic due to the effects of (1) or (2) above, or both. Increasing the anaerobic mass fraction during periods of low P removal was found to be counter-productive as this could be done only at the expense of the *anoxic* mass fraction which in turn gave rise to increased nitrate in the recycle.

After a year's endeavour, by the end of 1978 it was concluded that for the waste flows from Cape Town, treatment by the Phoredox type process was not suitable for excess P removal; this did not imply that the process might not be suitable for other waste flows but the investigation did bring to light that there were constraints, not adequately recognised before, that may prevent high P removals:

(1) For any selected sludge age and minimum temperature the requirement for efficient nitrification imposes an upper limit on the unaerated mass fraction.

(2) The limitation on the unaerated mass fraction correspondingly limits the concentration of nitrate that can be removed. If the nitrate generated is higher than the denitrification achievable, nitrate will appear in the effluent and, in the Phoredox system, the P removal will be adversely affected.

LATER DEVELOPMENTS

University of Cape Town Process (UCT Process)

From the findings on the Phoredox process it was clear that irrespective of other factors that may affect the excess P uptake, a major factor influencing the uptake is the presence of nitrate in the underflow recycle. If the nitrate content in the underflow to the reactor can be eliminated or kept at very low concentration, then there is a high expectation that excess P removal will be obtained. The principal obstacle to attaining this desirable end in the Phoredox process is that the nitrate discharged to the anaerobic reactor is linked directly to its concentration in the effluent. If for any reason the nitrate concentration increases with the COD remaining constant, i.e. if the influent TKN/COD ratio increases, the process offers little option to reduce this by operational means. The only operational means available is to reduce the magnitude of the underflow recycle but this is a risky option as the settleability of the mixed liquor in the plants tends to be poorer than in pure aerobic systems. Evidently a process configuration is needed that makes the anaerobic reactor independent of the effluent nitrate concentration. Towards this end, after a series of attempts, the configuration shown in Fig.5 was devised called the University of Cape Town process (UCT process).

In the UCT process, the settling tank underflow (s) recycle as well as the mixed liquor a-recycle are discharged to the anoxic reactor and an additional mixed liquor (r) recycle from the anoxic to the anaerobic reactor is introduced. The nitrate recycled to the anoxic reactor can be controlled by appropriately adjusting the mixed liquor a-recycle such that the nitrate concentration in the outflow of the anoxic reactor remains approximately zero. In consequence the mixed liquor r-recycle from the anoxic to the anaerobic reactor will contain very little or no nitrate and the anaerobic condition in the anaerobic reactor will be optimal.

Thus, *in the UCT process by application of an appropriate operational control strategy the anaerobic reactor can be maintained independent of the nitrate in the effluent even if the TKN concentration to the plant varies.*

Laboratory scale tests on the UCT process showed immediate improvement in excess P removal in both the concentration removed and the consistency in removal over those obtained in the Phoredox process. But perhaps the most important achievement, from a research point of view, was that with the UCT process it was now possible to eliminate the confounding effect of the nitrate in the recycle flow to the anaerobic reactor on excess P removal so that other factors influencing the excess removal could be investigated with greater ease. In the experimental response data the effects of these other factors now became clearly evident:

(1) For the same influent COD, one batch of sewage gave high removals, another gave low, an observation previously surmised but not explicitly identified due to the difficulty of isolating this effect when nitrate was recycled to the anaerobic reactor.

(2) Generally as the storage time of a batch of sewage (at 5°C) increased, both the excess P removal and the nitrate removal declined. Evidently on storage a progressive change was taking place in the constitution of the sewage which acted adversely on the two phenomena; direct evidence of change was indicated by the gradual reduction of COD of the batch during storage.

Identification of the factors in the sewage that influenced P removal proved to be a long and tedious undertaking; any success eventually attained can be ascribed wholly to having available the general nitrification-denitrification kinetic activated sludge model. To describe the developments in excess P removal and *inter alia* to give answers to the apparently erratic behaviour mentioned above, it is necessary to review briefly those aspects in the general theory that assisted in developing a solution.

Denitrification Aspects

A general aerobic kinetic model for the activated sludge process, including nitrification, was presented by Dold, Ekama and Marais (1980). Van Haandel, Ekama and Marais (1981) extended the model to include the kinetics of denitrification. The extended model, when calibrated, was found to describe the response of the multi-reactor nitrification-denitrification activated sludge process with unexpectedly good accuracy, under any cyclic influent flow and COD and TKN load patterns, both at laboratory, (van Haandel *et al.*, 1981) and at full scale, (Nicholls, 1982).

There are two basic aspects, *inter alia*, in which this model differs from previous activated sludge models, (1) the influent COD, S_{ti}, is divided into a number of fractions, unbiodegradable soluble, $S_{usi} = f_{us}.S_{ti}$, unbiodegradable particulate $S_{upi} = f_{up}.S_{ti}$ and biodegradable $S_{bi} = (1-f_{up}-f_{us})S_{ti}$. The biodegradable fraction, S_{bi}, in turn is subdivided into two fractions, (i) rapidly biodegradable soluble $S_{bsi} = f_{bs}.S_{bi}$ and (ii) slowly biodegradable particulate $S_{bpi} = (1-f_{bs})S_{bi}$. The two biodegradable fractions are metabolised by respective mechanisms that differ substantially, the rapidly biodegradable soluble fraction being absorbed directly and the slowly biodegradable particulate requiring adsorption and extra-cellular enzymatic breakdown prior to absorption, the two mechanisms being modelled by the Monod and the Levenspiel active-site type reaction rates respectively. (2) The classical synthesis-endogenous respiration approach to modelling bacterial growth kinetics is discarded in favour of a growth-death model. In this model only growth and death is recognized, no maintenance energy *per se*. On death the organism lyses its energy in the form of slowly biodegradable particulate COD to the bulk liquid, to add to the energy entering the system via the influent flow. Recognition of the bi-substrate and growth-death hypotheses formed the basis for developing an integrated model to describe the process response under anaerobic, anoxic and aerobic conditions in the activated sludge process and eventually, formed the basis also for a heuristic quantitative description of the excess P removal phenomenon.

By means of the extended model, under constant flow and load conditions, the two phase behaviour of denitrification in the pre-D reactor and the single phase behaviour of denitrification in the post-D reactor could be accurately reproduced and it was demonstrated that the first phase in the pre-D reactor is due solely to the rapidly biodegradable COD, the second phase in the pre-D and the single phase in the post-D reactors due to the slowly biodegradable particulate COD. In this fashion the formerly empiric relationship for denitrification, Eq.(1), was given a fundamental basis. From the behaviour of the general model it was possible also to develop simple equations to describe the nitrification behaviour in the multi-reactor nitrification-denitrification system under constant flow and load conditions. The nitrification and denitrification behaviour as predicted by the simple equations were found to be very close to that predicted by the general model (van Haandel, Dold and Marais 1982).

Using the simple nitrification and denitrification equations described above two mass parameters were developed which assist considerably in appreciating the behaviour of nitrification-denitrification systems, i.e. (1) the *nitrification capacity* which is the maximum mass concentration of nitrate (with respect to the influent) the aerobic reactors can generate, and (2) the *denitrification potential* which is the maximum mass of nitrate (with respect to the influent) an unaerated reactor can denitrify if nitrate is always present in the reactor and in the effluent from the reactor. If insufficient nitrate is recycled to the unaerated reactor the full potential for denitrification cannot be developed and the *denitrification performance* or *denitrification capacity* is less than the potential.

The nitrification capacity and denitrification potential are dependent principally on the influent TKN and influent COD concentrations respectively. Consequently, the influent TKN/COD concentration ratio forms a rough relative measure of the ratio of the mass of nitrate produced to the mass of nitrate denitrified and its magnitude forms a useful reference parameter against which the nitrification-denitrification behaviour of the various processes can be assessed. In evaluating the Bardenpho process, van Haandel *et al.*, (1982) developed explicit equations which, for any selected wastewater characteristics (i.e. μ_{nm20}, T_{max} and T_{min}, f_{up}, f_{us} and f_{bs}) and process characteristics (i.e. sludge age R_s, sludge underflow s- and mixed liquor a-recycle ratios), give the maximum TKN/COD ratio*, the maximum unaerated sludge mass fraction (f_{xm}) and the optimal division of f_{xm} into pre- and post-D sludge mass fractions (f_{x1}, f_{x3}) for complete denitrification. By performing the calculation for a range of sludge ages and noting the upper limitation on f_{xm} of 0,50 (and some other minor ones), design curves can be drawn. Figure 7 gives examples of such curves for 14°C and 20°C; raw wastewater characteristics $\mu_{nm20} = 0{,}36(1{,}123)^{(T-20)}/d$, $f_{up} = 0{,}13$, $f_{us} = 0{,}10$ and $f_{bs} = 0{,}24$ and process characteristics s = 1, a = 2,4,6 and 8 at 20°C and 4 at 14°C and the factor of safety for nitrification $S_f = 1{,}25$. Figure 7 clearly illustrates the effect of sludge age on (i) the maximum TKN/COD ratio with which the Bardenpho process can achieve complete denitrification at the two temperatures, (ii) the maximum allowable unaerated sludge mass fraction (f_{xm}), (iii) the division of f_{xm} between the pre-D (f_{x1}) and post-D (f_{x3}) reactors, and (iv) the effect of different a-recycle ratios. Note that the maximum TKN/COD ratio is not increased very much by increasing the a-recycle ratio above 4.

Selection of a Bardenpho process is indicated only if a horizontal line drawn at the expected influent TKN/COD intersects the TKN/COD vs R_s curve for complete denitrification, for the lowest temperature expected, in which event the intersection point defines the minimum sludge age to be used. If no intersection occurs the Bardenpho process cannot achieve complete denitrification and the MLE process should be selected. When a Bardenpho process is possible, the sludge age should be chosen longer than the indicated minimum to provide greater security in achieving complete denitrification.

*The TKN/COD ratio is not calculated directly but derived by a very close approximation from the (nitrification capacity)/(biodegradable COD) ratio.

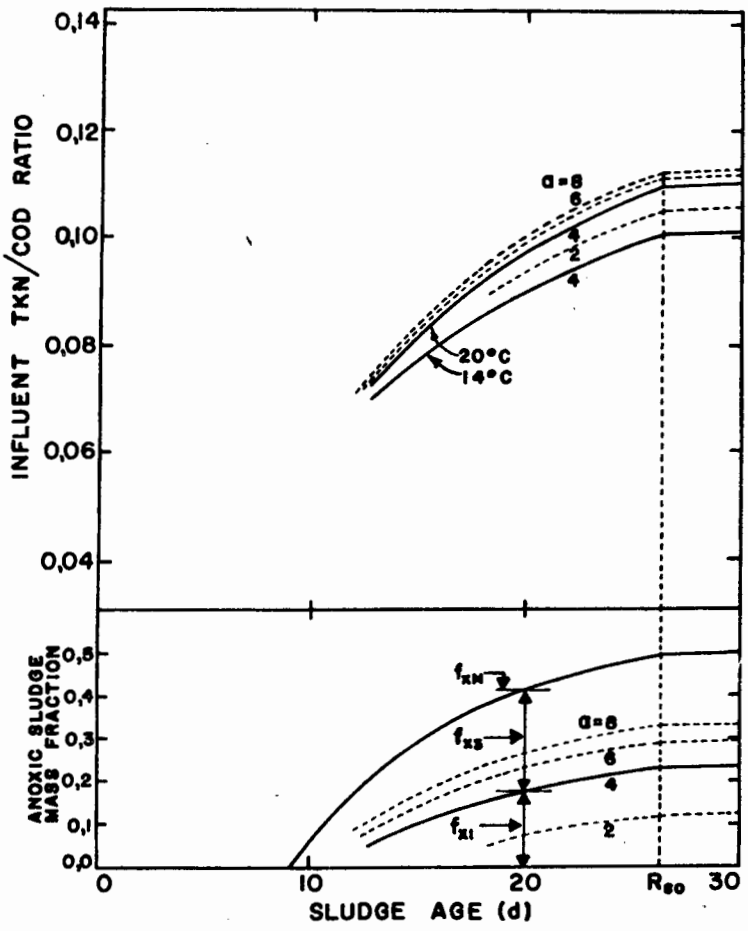

Fig.7. Maximum influent TKN/COD ratio, maximum unaerated sludge mass fraction f_{xm}, pre-D and post-D sludge mass fractions (f_{x1}, f_{x3}) respectively versus sludge age for the Bardenpho 4 stage nitrification-denitrification processes operating between 14°C and 20°C at mixed liquor a-recycle ratios of 2,4,6 and 8. (μ_{nm20} = 0,36/d, μ_{nm14} = 0,18/d, S_f = 1,25, s=1, f_{xm}max.= 0,50, raw wastewater with f_{us} = 0,10, f_{up} = 0,13 and f_{bs} = 0,24).

It should be noted in Fig.7 that there is a maximum sludge age (R_{so}) beyond which the maximum TKN/COD ratio for complete denitrification does not increase, i.e. about 28 days (for the sewage characteristic, etc. in the plot) at which the maximum TKN/COD ratio is 0,10 mgN/mgCOD. This maximum occurs when f_{xm} has reached its limit of 0,50. Hence to achieve complete denitrification for TKN/COD ratios of 0,10 mgN/mgCOD requires very long sludge ages, which makes the process volume per unit COD load very large. If the sludge age is restricted to say 20 days for economic reasons, the maximum TKN/COD ratio with which complete denitrification can be achieved reduces to 0,09 mgN/mgCOD at 14°C.(Fig.7).

Phoredox Process Analysis

Siebritz, Ekama and Marais (1980) extended the analysis of the Bardenpho process described above to the Phoredox process. In this process, a certain fraction (f_{xa}) of the total unaerated sludge mass fraction (f_{xt}) is "set aside" as an anaerobic reactor to establish the prerequisites for excess phosphorus removal. Only the remaining unaerated sludge mass fraction (f_{xt}-f_{xa}) is available as pre- and post-D reactors for nitrogen removal. If no nitrate is to be recycled to the anaerobic reactor (to ensure the most "intense" anaerobic condition) then complete denitrification must be achieved in the anoxic sludge mass fraction (f_{xt}-f_{xa}). The denitrification behaviour of the anoxic reactors in the Phoredox process for complete denitrification is the same as those in the Bardenpho process for complete denitri-

fication. However for the same f_{xt}, the Phoredox process has less anoxic sludge mass available for denitrification than the Bardenpho process due to the presence of the anaerobic reactor. Hence, to obtain complete denitrification in the Phoredox process, the maximum TKN/COD ratio necessarily must be lower than that for complete denitrification in the Bardenpho process. By extending the example of the Bardenpho process given above (Fig.7) to the Phoredox process with f_{xa} = 0,15, a maximum TKN/COD ratio of 0,09 mgN/mgCOD is found for 28 days sludge age and 0,08 mgN/mgCOD for 20 days sludge age, both at 14°C. If the TKN/COD ratio of the influent to a Phoredox process exceeds these limits, complete denitrification is unlikely to be obtained, resulting in nitrate in the effluent and underflow s-recycle; nitrate discharged to the anaerobic reactor via the s-recycle will cause a decline in P removal. From a design point of view, the TKN/COD ratio limits should be reduced to provide a factor of safety for denitrification, in which event the limits are probably nearer 0,07 to 0,08 mgN/mgCOD for sludge ages of 20 and 30 days at 14°C respectively.

The upper limit of the TKN/COD ratio of 0,07 to 0,08 mgN/mgCOD for successful operation of the Phoredox process severely restricts application of the process in the treatment of municipal wastewaters because the influent TKN/COD ratios of raw wastewaters range between 0,07 to 0,09 mgN/mgCOD, and of settled wastewaters generally are greater than 0,10 mgN/mgCOD.

UCT Process Analysis

An analysis of the UCT process showed that for this process also there is an upper limit to the TKN/COD ratio for excess P removal. At a TKN/COD ratio of about 0,14 mgN/mgCOD (at 14°C and 25 days sludge age) the nitrate concentration in the effluent and hence in the underflow s-recycle (s=1) is so high that this recycle by itself fully loads the anoxic reactor to its denitrification potential, i.e. the mixed liquor a-recycle needs to be reduced to zero. Hence at TKN/COD ratios >0,14 mgN/mgCOD, nitrate will be present in the pre-D reactor, and the discharge of nitrate to the anaerobic reactor cannot be avoided leading to a decline in excess P removal. However the 0,14 mgN/mgCOD TKN/COD ratio limit for the UCT process is considerably higher than 0,08 mgN/mgCOD limit for the Phoredox process and is above that for most settled and raw municipal wastewaters which generally range between 0,07 to 0,11 mgN/mgCOD.

Modified UCT Process

Experience with the UCT process brought to light a different type of problem that could greatly affect the successful operation of the process. In the process, as the TKN/COD ratio increases, the a-recycle ratio needs to be reduced to avoid nitrate discharge to the anaerobic reactor. A reduction in the a-recycle ratio causes an increase in the *actual anoxic* retention time. It was found that for high influent COD concentrations (>500 mgCOD/ℓ) and TKN/COD ratios >0,11 mgN/mgCOD, the actual anoxic retention time was greater than 1 hour. From experimental results, there are strong indications that when the actual anoxic retention time increases above about 1 hour, the settleability of the mixed liquor sharply declines.* One now faces a situation in which the process will operate satisfactorily with respect to P removal but may fail due to settleability problems, or if the secondary settling tanks are designed to cope with the poor settling sludge, inordinately large settling tanks will be required. Consequently, in design to preserve good settleability, *an upper limit of 1 hour must be imposed on the actual anoxic retention time*. This limitation creates a conflict between good P removal and good settleability for TKN/COD ratios >0,10 to 0,11 mgN/mgCOD (depending on the COD strength of the wastewater) because the former demands a low a-recycle ratio and the latter a high one. The problem was overcome by making a modification to the UCT process.

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*For reasons not yet understood the anaerobic retention time, both nominal and actual does *not* appear to affect the settleability of the sludge.

In the modified UCT process (Fig 6), the anoxic is subdivided into two parts, the first having a sludge mass fraction of 0,07 to 0,10 (depending on the influent COD concentration) and the second having the balance of the anoxic sludge mass fraction available. The first anoxic reactor receives the underflow s-recycle and the r-recycle to the anaerobic reactor is taken from it. The second anoxic reactor receives the a-recycle. This process allows operation of a-recycle ratios resulting in actual anoxic retention times less than 1 hour while ensuring a nitrate free discharge to the anaerobic reactor. An added advantage of this process over the UCT process is that it obviates the need for careful control of the a-recycle ratio to ensure a nitrate free discharge to the anaerobic reactor.

Application of the modified UCT process gave the most consistent P removal and the best settleability of all the processes investigated, but the improvements are obtained at a cost: the maximum TKN/COD ratio to give a zero nitrate discharge to the anaerobic reactor is reduced from 0,14 mgN/mgCOD in the UCT process to 0,11 mgN/mgCOD in the modified UCT process. However a TKN/COD ratio of 0,11 mgN/mgCOD includes most settled and raw municipal wastewaters. Furthermore, by making provision that the r-recycle can be taken from either the first or second anoxic reactor, the process can be operated either as a modified UCT or a UCT process as may be required.

The developments that have been described so far were all guided by the hypothesis that excess P removal is stimulated, and is best achieved, by having an anaerobic reactor and that it is optimized by preventing nitrate from entering the reactor. No information has been put forward to quantify firstly, the conditions in the anaerobic reactor that cause the stimulation and, secondly, the magnitude of the excess P removal to be expected. The rest of this paper will be concerned with these two aspects.

PREREQUISITES FOR EXCESS PHOSPHORUS REMOVAL

The improved understanding of the nitrogen removal process behaviour led to a new approach in investigating the prerequisites in the anaerobic reactor for excess phosphorus removal. Ekama, van Haandel and Marais (1979) hypothesized that if the mass of nitrate entering an unaerated reactor is less than that reactor's denitrification potential, the difference defines an "*anaerobic capacity*" in the reactor. They speculated that this anaerobic capacity could substitute for the redox potential level (suggested by Barnard, 1976) as a measure for predicting when phosphorus release takes place in the anaerobic reactor. Siebritz, *et al.* (1980) intensively investigated this hypothesis. They plotted the P release in the anaerobic reactor, the P uptake in the aerobic reactor and the system P removal versus the anaerobic capacity (A_C) for data from UCT and modified Phoredox processes (Fig.8). This plot shows that (i) if $A_C < 10$ mgNO_3-N/ℓ, no P release in the anaerobic reactor is obtained; in fact, P uptake is noted, (ii) when $A_C > 10$ mgNO_3-N/ℓ, P release is obtained, and (iii) as A_C increases above 10 mgNO_3-N/ℓ so the P release in the anaerobic reactor, the P uptake in the aerobic reactor and the system P removal increase.

The data in Fig.8 appeared to support the anaerobic capacity hypothesis. Consequently if the anaerobic hypothesis is correct, then provided this capacity can be induced in any system other than the UCT and Phoredox processes, P release and uptake should be observed.

To test the above conclusion experimentally, three Modified Ludzack-Ettinger (MLE) processes (Fig 4) and a modified UCT process were set up and fed from the same wastewater source. The three MLE units were given unaerated sludge mass fractions of 40, 55 and 70 percent respectively and the mixed liquor a-recycle ratios were set such that the anaerobic capacities ranged from 6 to 35 mgNO_3-N/ℓ in the anoxic reactors. Over two months of operation no P release nor excess P removal were observed in any of the MLE units. In contrast, the modified UCT process with a 0,10 anaerobic sludge mass fraction, consistently gave P release and excess P removal. It was concluded from these results that the anaerobic capacity hypothesis is not

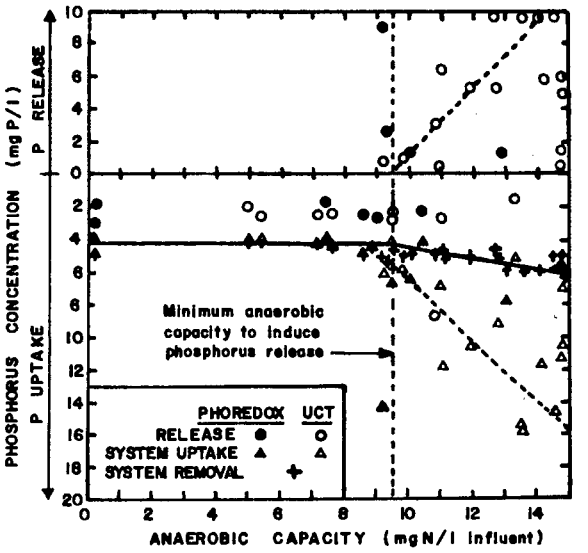

Fig.8. P release in the anaerobic reactor, process P uptake and process P removal versus the anaerobic capacity of the anaerobic reactor (A_c) for the modified Phoredox and UCT processes.

sustained.

In seeking an explanation for the different P release behavioural patterns in the modified UCT and MLE processes, it was noted that the only evident difference lay in the concentration of rapidly biodegradable COD surrounding the organisms in the anaerobic reactor (S_{bsa}). In the modified UCT process the rapidly biodegradable COD concentration in the anaerobic reactor (S_{bsa}) is the maximum possible as no nitrate is recycled to the anaerobic reactor; in contrast, in the MLE process sufficient nitrate is recycled to the anoxic reactor to utilize all the rapidly biodegradable COD i.e. $S_{bsa} = 0,0$. Therefore the different behavioural patterns of the processes would be consistently described if it is assumed that the concentration of rapidly biodegradable COD in the anaerobic reactor (S_{bsa}) surrounding the organisms is the key parameter determining whether or not P release and excess P uptake takes place.

To test the assumption above, it was necessary to develop a general equation by means of which S_{bsa} can be calculated:

Consider the anaerobic reactor in the UCT process,

$$S_{bsa} = (f_{bs}\ S_{bi} - \Delta S_{bs})/(1+r)\ (mgCOD/\ell) \qquad (2)$$

The term S_{bs} is the concentration of rapidly biodegradable COD utilized for synthesis of cell material with nitrate (introduced via the r-recycle) and dissolved oxygen (introduced via the influent) serving as terminal electron acceptors. Because 8,6 mgCOD are utilized with the removal of 1 mgNO_3-N (van Haandel, Ekama and Marais, 1981) and 3,0 mgCOD with 1 mgO. (Marais and Ekama, 1976), ΔS_{bs} can be expressed in terms of the nitrate in the r-recycle, N_{nr}, and the D.O. in the influent (d_i) and r-recycle (d_r), i.e.

$$\Delta S_{bs} = 8,6.r.N_{nr} + 3,0\ (d_i + r.d_r) \qquad (3)$$

Equations (2 and 3) can be easily adapted for the other processes by giving due consideration to the recycles and flows discharged to the anaerobic reactor.

The calculation of S_{bsa} fortunately was possible because once the importance of the influent rapidly biodegradable COD fraction (f_{bs}) was recognized from the work on

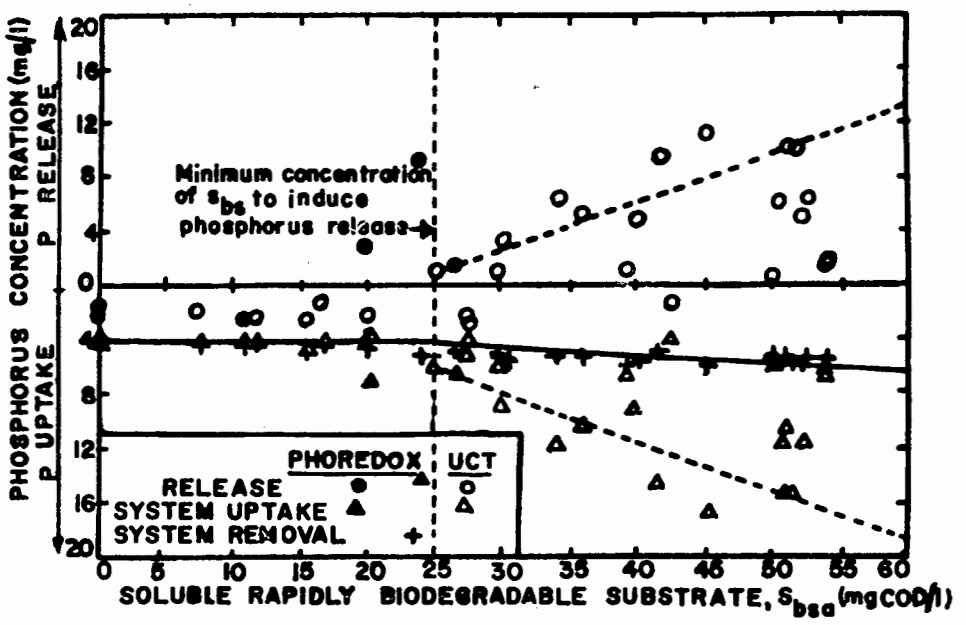

Fig.9. P release in the anaerobic reactor, process P uptake and process P removal versus rapidly biodegradable COD concentration in the anaerobic (S_{bsa}) for the modified Phoredox and UCT processes.

denitrification, it became standard experimental procedure to measure or determine almost daily, f_{bs}, f_{us}, f_{up}, S_{ti}, N_{nr}, d_e and d_i. Consequently Eqs.(2 and 3) were applied to the data used to plot Fig.8 and replotted in Fig.9 with S_{bsa} on the horizontal axis instead of the anaerobic capacity. From Fig.9 the following conclusions were drawn:

1) The minimum rapidly biodegradable COD concentration in the anaerobic reactor (S_{bsa}) to stimulate phosphorus release in the reactor is about 25 mgCOD/ℓ.

2) The degree of P release appears to increase as S_{bsa} increases above 25 mgCOD/ℓ, i.e. P release increases as (S_{bsa}-25) increases.

3) Excess phosphorus uptake is obtained only when phosphorus release takes place, and tends to increase with (S_{bsa}-25).

The plots in Figs.8 and 9 show a striking similarity but on closer inspection, this similarity is more apparent than real. The similarity is there only for the UCT and Phoredox data: for these processes, the two sets of data fall in approximately the same position relative to the coordinate axes. This is so because in these processes, the principal contributor to A_c is the rapidly biodegradable COD in the influent, S_{bsi} - the contribution by the slowly biodegradable influent COD S_{bpi} is very small owing to the relatively small anaerobic sludge mass fractions (f_{xa}) - so that A_c and S_{bsa} are essentially equivalent parameters. In contrast, in the MLE process, the influent rapidly biodegradable COD S_{bsi} will have been completely utilized by the nitrate entering the anoxic reactor, i.e. S_{bsa} = 0. Nevertheless high A_c values are obtained from the S_{bpi} contribution because the unaerated sludge mass fractions are large. Consequently for the MLE process, there is no relationship between S_{bsa} and A_c. Hence in Fig.8, the MLE data fall in the right hand side of the plot (i.e. A_c >10 mgNO_3-M/ℓ) whereas in Fig.9 they will fall in the left hand side of the plot (i.e. S_{bsa} = 0). Consequently, the MLE behaviour is incorrectly predicted by the A_c hypothesis (Fig.8) but correctly predicted by the S_{bsa} hypothesis (Fig.9). These results allow the following statement to be made: A prerequisite for P release in the anaerobic reactor is that the concentration of rapidly biodegradable COD surrounding the organisms in the anaerobic reactor must exceed approximately 25 mgCOD/ℓ.

MAGNITUDE OF EXCESS PHOSPHORUS REMOVAL

A prerequisite for P release was stated above. However, the magnitudes of the P release and subsequent uptake and removal were not explicitly defined, once the prerequisite was satisfied. For this purpose an extensive and intensive investigation was inaugurated utilizing the UCT and modified UCT configurations. Series of tests were done under constant flow and load conditions: (1) at 14°C and 20°C, (2) using raw wastewater influents with COD's of 800, 500 and 300 mg/ℓ, and (3) varying the r-recycle and anaerobic mass fraction. In all the investigations the influent wastewater characteristics, i.e. COD, TKN, total P and rapidly biodegradable COD fraction f_{bs}, and filtered TKN, NH_4^+, NO_3^- and total P in the process reactors were measured daily. In addition, all the normal parameters such as MLVSS, oxygen utilization rate, stirred settling velocity, pH and alkalinity were measured at regular intervals.

An analysis of these data* indicated that provided S_{bsa} >25 mgCOD/ℓ,

1) for fixed r-recycle ratio and influent COD, increasing the volume of the anaerobic reactor (at the expense of the other reactor volumes) tended to increase P release and the P removal,

2) for fixed r-recycle ratio and anaerobic reactor volume, an increase in influent COD concentration tended to increase the P release and the P removal.

Although the trends stated above were evident it was not possible to identify a consistent behavioural pattern and it was concluded that the basic parameters had not been properly identified or isolated. In part, this was due to the interactive effects between the different parameters, for example, increasing the r-recycle ratio, (i) increases the mass of sludge passing through the anaerobic reactor, (ii) decreases the time the sludge is retained in the anaerobic reactor, (iii) increases the concentration of sludge in the reactor, and (iv) decreases the concentration of S_{bsa} in the anaerobic reactor (even if no nitrate is present in the r-recycle). With so many associated changes it was difficult to see directly which parameters are the significant ones. It was decided, therefore, to investigate the system theoretically on the basis of the perceived and hypothesized behaviour.

Consideration of the P release in the anaerobic reactor indicated that the magnitude of the release was not a consistent parameter; experimental P release data showed that the release at any particular time depended on the P removal performance prior to the time the test was taken. If, for example, the prior removal was low the P release observed also was low; as the removal increased so in time the release did likewise and *vice versa*. For this reason the P release *per se*, was not incorporated in the analysis and attention was focussed on the excess P removal; here the following behavioural pattern was hypothesized based on the observed behaviour,

1) Excess P removal is obtained only when S_{bsa} >25 mgCOD/ℓ.

2) As S_{bsa} increases above 25 mgCOD/ℓ, so the P removal increases.

3) The longer the *actual* anaerobic retention (R_{an}), the higher the P removal.

4) The larger the mass of sludge recycled through the anaerobic reactor, the higher the P removal.

Scrutiny of (4) above showed that it could be transformed to a more useful equivalent,

4) The greater the mass of sludge recycled through the anaerobic reactor each day expressed as a fraction of the mass of sludge in the process, n, the higher the P removal.

The statements (2) and (4) above do not give an explicit quantitative expression of

*Detailed description of the experimental investigation will be published in a later publication.

the expected behaviour. To obtain such an expression an hypothesis on the expected behavioural pattern of (2) to (4) has to be made. An hypothesis consistent with the observations is:

"When any one of the factors (S_{bsa}-25), R_{an}, or n, is zero, excess phosphorus removal will be zero."

From this hypothesis, the *simplest* form of an equation expressing the tendency of a process to achieve excess P removal is

$$P_f = (S_{bsa}-25).R_{an}.n \quad (4)$$

where

P_f = excess phosphorus removal propensity factor.

If P_f as defined above describes the observed behaviour of the three parameters, then the P removal due to excess uptake (ΔP_u) should be a function of P_f, i.e.

$$\Delta P_u = f(P_f) \quad (5)$$

Equation (4) can be expressed in terms of the process configuration and operational parameters. This is demonstrated below for the UCT process.

$$R_{an} = V_{an}/\{Q(1+r)\} \quad (6)$$

$$n = (rQ.X_{ax})/(V_t\bar{X}) \quad (7)$$

From a sludge mass balance around the anaerobic reactor it follows that

$$X_{ax} = \left(\frac{1+r}{r}\right) X_{an} \quad (8)$$

The anaerobic sludge mass fraction, f_{xa}, is given by

$$f_{xa} = (X_{an}.V_{an})/(\bar{X}.V_t)$$

$$= (X_{an}.f_{xav})/\bar{X}$$

where

$\bar{X}$ = mean sludge concentration in process

$$= (X_{an}.V_{an} + X_{ax}.V_{ax} + X_{ae}.V_{ae})/V_t \quad (9)$$

i.e. $$X_{an} = \bar{X}.(f_{xa}/f_{xav}) \quad (10)$$

Substituting Eq.10 into Eq.8 and Eq.8 into Eq.7;

$$n = (r.Q.(\frac{1+r}{r}).\frac{f_{xa}}{f_{xav}}.\bar{X})/(V_t\bar{X}) = \{Q(r+1)\ \frac{f_{xa}}{f_{xav}}\}/V_t \quad (11)$$

Multiplying Eq.11 by LHS and RHS of Eq.6

$$nR_{an} = \{Q(r+1)\ \frac{f_{xa}}{f_{xav}}\}\ \frac{1}{V_t}.\frac{V_{an}}{Q(r+1)} = f_{xa} \quad (12)$$

Substituting f_{xa} for nR_{an} in Eq.4

$$P_f = (S_{bsa}-25)f_{xa}\ \ (mgCOD/\ell) \quad (13)$$

Hence the propensity to give excess phosphorus removal appears to be a function only of the magnitude of S_{bsa} above 25 mgCOD/ℓ and the magnitude of the anaerobic sludge mass fraction.

Equation 12 can be shown to hold also for the Phoredox type processes.

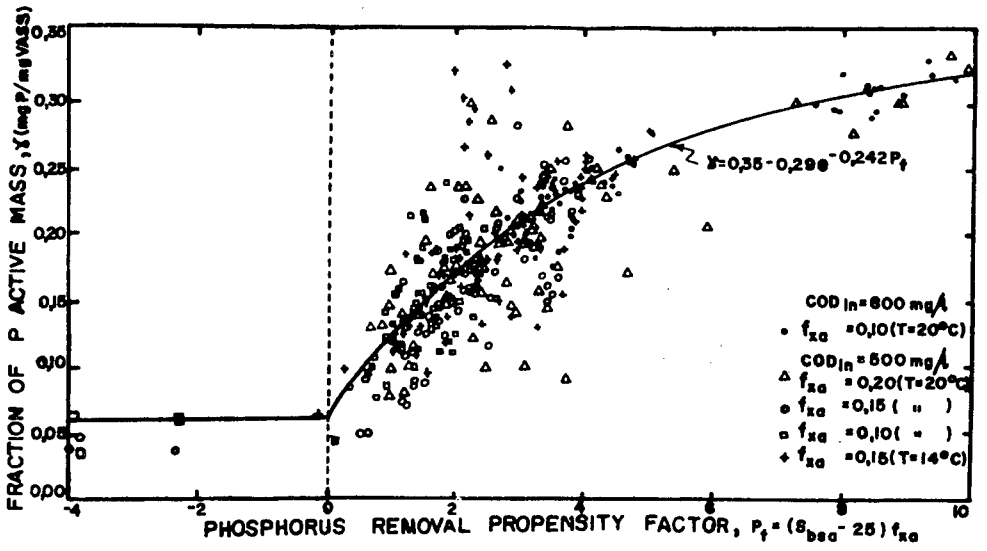

Fig.10. Coefficient of excess P removal (γ) versus P removal propensity factor (P_f) observed in the modified Phoredox, UCT and modified UCT processes at different anaerobic sludge mass fractions (f_{xa}), influent COD concentrations and temperatures.

QUANTITATIVE MODEL OF EXCESS PHOSPHORUS REMOVAL

As excess P removal is accepted to be a biological activity, it can be assumed that, (i) only the active fraction of the sludge can take up phosphorus in excess, (ii) the phosphorus removal will increase as the proportion of phosphorus in the active mass increases, and (iii) the proportion of phosphorus in the inert fractions of the sludge will remain unchanged. Accepting these assumptions, Martin and Marais (1975) developed the following equation for phosphorus removal based on the steady state activated sludge process model presented by Marais and Ekama (1976):

$$\Delta P_s = S_{ti}\left\{\frac{(1-f_{us}-f_{up})Y_h}{(1+b_{hT}R_s)}(\gamma+f_p f\, b_{hT}R_s) + \frac{f_p f_{up}}{P_v}\right\} \qquad (14)$$

With the aid of Eqs.2 and 3, 13 and 14, the coefficient of excess phosphorus removal and the propensity factor P_f were calculated for daily sets of experimental data* measured over a period of 18 months. In calculating the daily γ and P_f data pairs, those data for which there were known causes that may have adversely or favourably influenced the process behaviour were discarded.** The remaining daily γ and P_f data pairs are shown plotted in Fig.10.

The data in Fig.10 shows considerable scatter although a definite trend is discernable. The scatter is due mainly to the selection of the data values in the

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*The rapidly biodegradable COD fraction f_{bs} in the influent was measured in accordance with the procedure developed by Ekama and Marais (1978) as follows: A single completely mixed aerobic activated sludge unit is operated at 2,5 days sludge age. The wastewater is fed in a daily cyclic square wave loading pattern (12 hours on, 12 hours off). By measuring the precipitous decrease in oxygen consumption rate over the period of feed termination, the f_{bs} fraction can be readily ascertained.

**It was found that after a disruption of the process due to a mechanical breakdown, or a change in influent sewage characteristics or process parameter, the process required approximately 2 to 3 days to restabilize.

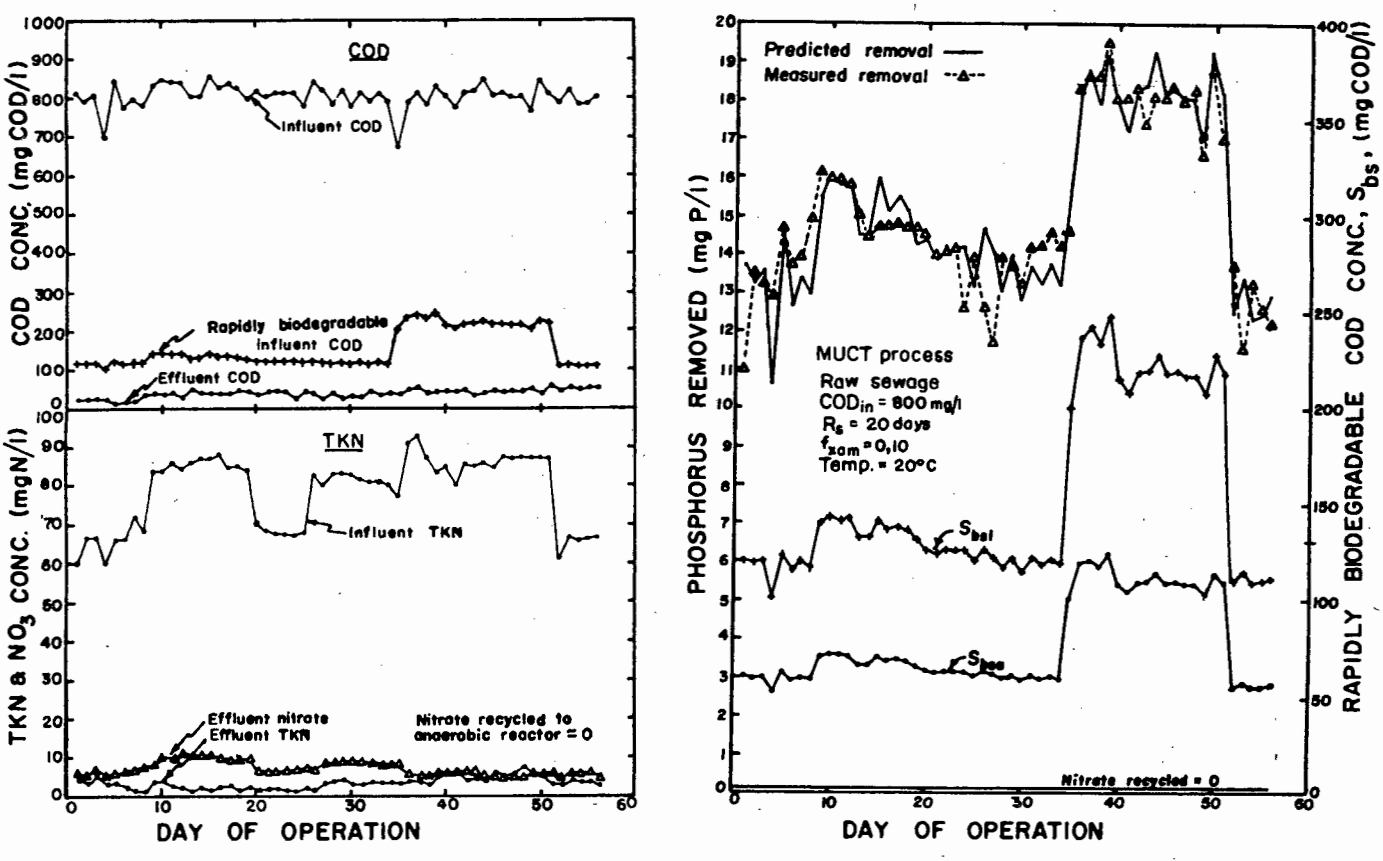

Fig.11. *Left*, daily experimental data of influent COD, TKN and rapidly biodegradable COD concentrations and nitrate concentrations in the effluent and the recycle to the anaerobic reactor and *right* the measured and predicted phosphorus removal for a modified UCT process with the following sludge mass fractions; anaerobic 0,10, first anoxic 0,08, second anoxic 0,22, aerobic 0,60.

calculation of P_f: The f_{bs}, nitrate and P removal values used in the calculations were all measured on the same day, i.e. the assumption was made that the response of γ to P_f is instantaneous. This, in fact, is not so; due to the long hold up time in the system it was repeatedly observed that the P removal response is out of phase with the input by some fraction of a day. (This is apparent in Fig.12 which records the observed and predicted P removal in one set of experiments).

Accepting the inevitable large scatter, the form of the relationship and the constraints on the γ-P_f relationship were derived as follows: From Fig.9 apparently

i) there is an upper limit to γ, of about 0,35 at very high propensity factors,

ii) there is a lower limit to γ of about 0,06 at a propensity factor of zero,

iii) for propensity factors ranging from infinity to zero the maximum change in is (0,35-0,06) = 0,29 and the decrease in γ with decrease in P_f appears to be of an exponential form.

On the basis of the above the following expression was chosen to represent the trend in the plotted data

$$\gamma = 0,35-0,29 \exp(-C.P_f) \qquad (15)$$

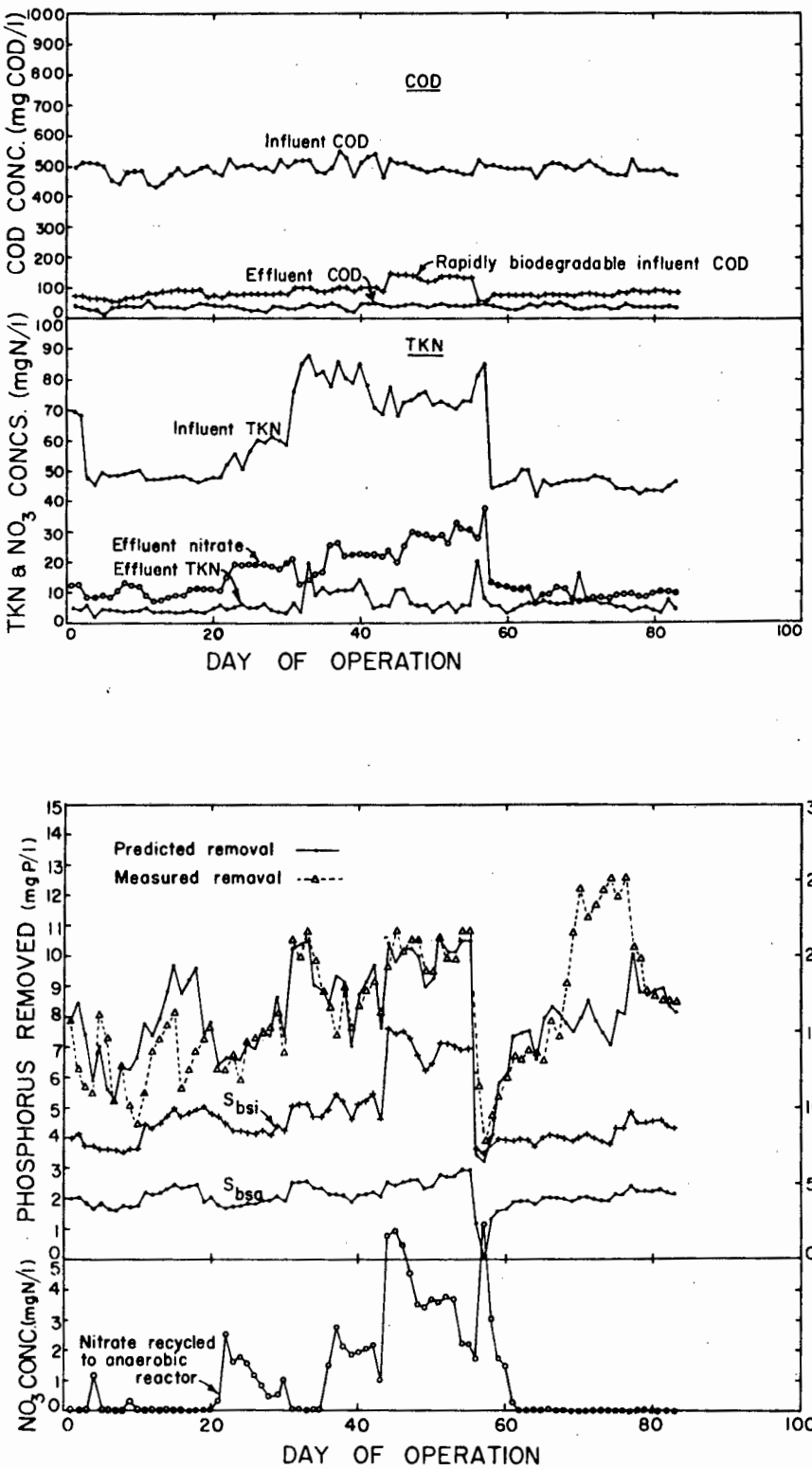

Fig.12. Response of a laboratory scale UCT process at 14°C, Anaerobic mass fraction = 0,15, Anoxic mass fraction 0,30. Aerobic mass fraction 0,55, Sludge age 20 days, treating unsettled flow from Mitchell's Plain.

The value of C was found by a least square analysis of the differences between the measured and predicted phosphorus removals and found to be equal to -0,242, i.e.

$$\gamma = 0{,}35-0{,}29.\exp(-0{,}242\ P_f) \quad (mgP/mgVASS) \qquad (16)$$

To check the predictive capacity of Eq.16, it was applied to the daily P_f data in all the five sets of experiments on the modified UCT, UCT and Phoredox processes in which S_{bsi} and the nitrate in the recycles were measured. (As stated above these sets of data covered influent COD values from 300 to 800 mg/ℓ at 14° and 20°C under a variety of TKN/COD ratios, anaerobic mass fractions from 0,10 to 0,20 and sludge ages 14 to 25 days. As an illustration two sets of data are shown in Figs. 11 and 12 together with the predicted P removal values. Evidently the model gives a good prediction of the observed P removal. In Fig.11, the pronounced favourable effect of an increase in the rapidly biodegradable COD concentration (S_{bsi}) on the P removal, and in Fig.12 the depressing effect of nitrate in the recycle to the anaerobic reactor, is clearly illustrated.

The theory was tested additionally by feeding extra rapidly biodegradable COD to the anaerobic reactor, acetate and glucose. Taking due account of the increased COD, again the predictions of P removal were in satisfactory correlation with those observed.

While doing a biodegradability investigation of the waste flow from the town of Caledon in South Africa, unexpected verification of the theory was obtained. The process configuration was a Modified Ludzack-Ettinger process (Fig.4) with an anoxic sludge mass fraction of 0,30 operated at 20 days sludge age, at 20°C, and with a mixed liquor (a) and an underflow (s) recycle ratio of 4:1 and 1:1 respectively. The wasteflow contained an industrial fraction (from a malting factory) constituting approximately 2/3 of the total COD load. The influent COD and TKN strengths were 1300 mg/ℓ and 70 mgN/ℓ respectively. It was found that the malting waste was virtually completely rapidly biodegradable resulting in a very high rapidly biodegradable COD fraction (f_{bs}) and concentration (S_{bsi}), 0,70 and 980 mgCOD/ℓ respectively. Taking due account of the diluting effect of the total recycle flow of 5 and the reduction of the rapidly biodegradable COD in the "anoxic" reactor by the nitrate discharged in the recycle flows (nitrification was complete, effluent TKN = 4 mgN/ℓ) the rapidly biodegradable COD concentration in the "anoxic" reactor (S_{bsa}) was estimated at 101 mgCOD/ℓ, the propensity factor (P_f) at 22,9 (Eq.13), the γ coefficient at 0,35 (Eq.15) to give an estimated P removal of 31 mgP/ℓ influent (Eq.14 with f_{us} = 0,05 and f_{up} = 0,06). The observed P removal was 29 mgP/ℓ. The results of this experiment should be contrasted with those discussed earlier on the Modified Ludzack-Ettinger processes. In these processes, no excess P removal was observed or predicted, even though the anoxic mass fraction was as high as 0,70, principally because the rapidly biodegradable COD concentration in the influent (S_{bsi}) was low and completely utilized in the anoxic reactor by the nitrate recycled to this reactor. Clearly if sufficient S_{bsi} is available and the TKN not excessive, it is possible to obtain high P removals even though the nitrate recycled to the anaerobic reactor is high, without having to resort to Phoredox or UCT configurations, provided the conditions for P release are satisfied as set out in this paper.

At full scale Nicholls (1982) tested the predictive power of the general nitrification-denitrification model on the Goudkoppies 5-stage Phoredox plant receiving an effluent that had passed through primary settling and then through an equalization tank. The P removal behaviour of the plant was also monitored by measuring P conditions in the anaerobic and aerobic reactors and in the effluent. To evaluate both the model and P removal theory, *inter alia* the rapidly biodegradable COD in the influent discharged to the process (S_{bsi}) was measured, as described by Dold, Ekama and Marais (1980). The S_{bsi} was found to be very low due to its utilization by an anaerobic sludge layer that formed on the bottom of the unstirred equalization tank. In terms of the theory set out here the S_{bsi} was so low that with the 1:1 underflow recycle from the secondary settling tank to the anaerobic reactor, even

if no nitrate was present in the recycle, S_{bsa} would be less than 25 mg/ℓ and consequently no excess P removal was to be expected, and, virtually no excess removal was observed for the plant. Measurements of S_{bsi} on the *influent* to the equalization tank however indicated that the S_{bsi} was sufficiently high that, if the equalization tank was bypassed, excess P removal was theoretically possible provided the nitrate in the underflow recycle to the anaerobic reactor could be maintained at less than 5 mgN/ℓ. Now at this point a computer-based equalization control strategy was implemented on the equalization tank (Dold, Buhr and Marais, 1982) and operated in such a fashion that any settled material was flushed daily from the tank. The flushing action prevented build-up of a sludge layer and effectively eliminated the loss of S_{bsi} in the tank. The process recycles in the plant were changed in accordance with those predicted by the general model to achieve maximum nitrate removal. As this removal was still insufficient to reduce the nitrate in the underflow recycle to less than 5 mgN/ℓ, the aerators next to the discharge points from the primary anoxic reactor were switched off, thereby effectively increasing the anoxic zone and further reducing the nitrate in the effluent. (Sufficient aerator capacity was available in the rest of the aeration basin not to affect the nitrification efficiency). In this fashion the nitrate was kept between 3 and 5 mgN/ℓ in the effluent and the underflow recycle. Under these conditions the predicted P removal was 4 to 5 mgP/ℓ influent; observed mean removal was 5 mgP/ℓ. The results from this investigation are particularly instructive because they verified that no P removal is achievable if S_{bsi} is too low, or, where S_{bsi} is sufficiently high although the potential for removal is there, it will not be possible to realise this potential if nitrate in the anaerobic recycle is so high that it reduces the S_{bsa} concentration to below the critical level.

When investigating P removal behaviour in laboratory scale processes, batches of sewage usually are obtained from the outfall sewer and stored at 5°C for subsequent feed to the laboratory process units. Often it will be noticed that with time the magnitudes of denitrification and P removal decline while feeding from the same raw sewage batch. Measurement of the rapidly biodegradable COD fraction of the daily feed taken from the cold storage batch has indicated that normally there is a slow continuous loss of this fraction. Theoretically the model accounts for the reduction in denitrification and P removal observed. Hence, batches should not be stored longer than about one to one and a half weeks and the S_{bsi} in the feed should be measured daily. Furthermore, by monitoring the S_{bsi} on a routine basis, changes in S_{bsi} between batches are picked up that explain the "erratic" P removal behaviour noted earlier between different batches of wastewater. Also, it is vitally important that the tanker transporting the batch to the laboratory and the cold storage tank are thoroughly cleaned between batches otherwise hydrogen sulfide generation and rapid loss of S_{bsi} will be encountered. High hydrogen sulfide concentration in the feed to a process can have severe adverse effects on the process response.

Reviewing the model in its entirety, it would appear that the P removal model gives predictions very consistent with those observed. This does not imply in any manner that the model has achieved finality; findings on the biochemical mechanism discussed by Marais *et al.* (1982) provide new directions for research and these may significantly modify the parametric model proposed here.

IMPLICATIONS OF THE PHOSPHORUS REMOVAL THEORY

Lack of space limits detailed discussion of all the aspects and implications of the P removal theory developed above. However brief mention of the following is merited:

(1) The magnitude of P removal per unit influent COD declines as the influent COD decreases. The main reason for this is that the concentration of rapidly biodegradable COD concentration, S_{bsi}, decreased concomitantly with decrease in total influent COD concentration. For raw municipal wastewater the fraction

of rapidly biodegradable COD (S_{bsi}) with respect to the total COD (S_{ti}) is about 0,2; consequently, when S_{ti} decreases to about 250 mg/ℓ, S_{bsi} decreases to 50 mg/ℓ so that for r = 1, even if no nitrate is recycled to the anaerobic reactor, S_{bsa} = 25 mg/ℓ, hence, $(S_{bsa}-25)\cong 0$, and no excess removal can be expected ($\gamma\cong 0,06$). Generally (for $S_{ti}>250$) as S_{ti} increases so the P removal per unit influent COD increases and the removal becomes less sensitive to external factors. Because P_f (and hence γ) is dependent on both $(S_{bsa}-25)$ and f_{xa}, P removal for any particular $(S_{bsa}-25)$ can be improved by increasing the anaerobic sludge mass fraction f_{xa}. This often is necessary for low S_{ti}. Values of f_{xa} up to 0,2 have been tested. However as f_{xa} increases so nitrate removal reduces unit per influent COD. The reason for this is that the total unaerated mass fraction (f_{xt}) is limited to 0,5 so that an increase in f_{xa} necessarily must reduce the anoxic mass fraction.

(2) Any practice that reduces S_{bsi} should be avoided. For example, recycling of excess underflow liquor to a point prior to the primary settling tank, to improve settleability,is to be avoided as any oxygen present in the influent, introduced by say archimedian screw pumps, will cause that the S_{bsi} be reduced by an amount equal to 3 times the oxygen introduced (see Eq.3). Conversely, any practice that increases S_{bsi} will improve P removal. For example, the Johannesburg City Council has augmented S_{bsi} as follows: the primary settling tank underflow is digested at very short sludge ages to produce fatty acids, the digested mixed liquor is settled and the fatty acid rich supernatant is fed to the P removal plant. The principal fatty acid produced is acetic acid - which is a most rapidly biodegradable COD source; this raises the S_{bsi} value of the influent and consequently will raise the magnitude of excess P removal. This innovation holds promise by providing a means to extend the P removal control over the plant, particularly where high P removal per unit influent COD is needed and when this removal is not attainable using the raw influent sewage as the only source of rapidly biodegradable COD.

(3) Cyclic flow and load conditions do not appear to affect the mean daily excess P removal, in fact, the removal often is improved, particularly under low average influent COD conditions. The reason for this improvement is that under the cyclic conditions (with constant recycle flows) during the peak periods the peak COD is higher than the daily mean causing a higher $(S_{bsa}-25)$ condition and hence higher P removals during the associated high flow period. However, under cyclic flow conditions the oxygen concentration in the aerobic reactor must be closely controlled; too high D.O. concentration reduces the nitrate removal whereas too low concentration may inhibit nitrification and adversely affect settling. The practical difficulties associated with oxygen control are such that serious consideration should be given to equalization tanks operated under a control strategy that equalizes *both* flow and load. Such a strategy is now available (Dold, Buhr and Marais,1982).

With regard to design, the following important considerations deserve mention:

(1) For design of nutrient removal plants the influent wastewater characteristics (or their ranges) need to be known with much greater surety than for conventional activated sludge plants otherwise a design may be produced that fails totally in its P removal objectives. Vital influent characteristics are (i) S_{ti}, TKN/COD, P/COD, S_{bi}, S_{bsi}, μ_{nm20}, T_{max} and T_{min}. Useful data are the Total Alkalinity and the unbiodegradable COD fractions f_{us} and f_{up}. In the event that these characteristics are known only approximately, values should be selected that lead to conservative designs, usually at the cost of reduced N and P removal.

(2) The selected process must have factors of safety built into it or have flexibility in operation, so that if the influent characteristics are more adverse than accepted for design, it will be possible to accommodate them. For example, if a Phoredox process is selected it is recommended that normally the

maximum TKN/COD ratio should not exceed 0,07 mgN/mgCOD, and the process should have a built-in safety factor by designing it for 0,08 mgN/mgCOD. For TKN/COD ratios > 0,07 mgN/mgCOD, the modified UCT/UCT* process should be selected; with this process combination, by appropriate regulation of the a-recycle ratio, excess P removal always can be induced (subject to S_{bsi}) at the cost of a reduced nitrogen removal. Theoretically, at low TKN/COD ratios (≅0,08), the Phoredox process will be the optimal one, but practically its inflexibility to accommodate TKN/COD ratio variations, makes its selection a risky one.

(3) The selected process should require the least amount of decision making from the operator to obtain consistent results. In this regard the modified UCT process appears to lend itself most readily to setting operational procedures to absorb adverse conditions when these arise. Also operational adjustment to mitigate the regular changes in wastewater flow and characteristics observed over different days of the week can be preprogrammed.

GENERAL CONCLUSIONS

This paper presented evidence that

(1) A prerequisite for P release under anaerobic conditions is that the concentration of rapidly biodegradable COD (similar to glucose or acetate) surrounding the organisms must exceed some minimum critical concentration (±25 mg/ℓ). P release appears to serve as an indicator that the organism mass has been conditioned to take up the released and additional P when subsequently aerated. Particulate slowly biodegradable COD does not appear to influence the release or excess uptake other than it contributes to active mass production which performs the P release and uptake.

(2) The magnitude of the excess biological P removal per unit of active mass of sludge (as VASS) under constant flow and load conditions is determined by (i) the actual mean retention time of the organisms in the anaerobic reactor, (ii) the fraction of the sludge mass in the system recycled through the anaerobic reactor each day, and (iii) the concentration of rapidly biodegradable COD in excess of 25 mgCOD/ℓ.

(3) The mass of P removed per day per unit COD load by a process is dependent on the mass of excess active sludge produced per day times the magnitude of the excess removal coefficient induced by (2) above. Consequently, the shorter the sludge age, the greater the removal of P per unit COD load.

(4) The source of the rapidly biodegradable COD is the influent wastewater and consists of about 20 percent of the influent COD in unsettled municipal wasteflows. The concentration of rapidly biodegradable COD in the anaerobic reactor is reduced by any nitrate recycled to this reactor (1 mg(NO_3-N) removes 8,6 mgCOD) and thereby reduces the excess P removal, to zero if the nitrate discharged is high enough.

(5) Analysis of the Phoredox process with respect to its nitrification and denitrification capacities and excess P removal, indicates that complete denitrification normally cannot be guaranteed if the influent TKN/COD ratio is greater than about 0,08 (for temperatures not falling below 12 to 14°C). At higher TKN/COD ratios nitrate will be present in the effluent and hence in the underflow recycle to the anaerobic reactor in which event excess P removal will decline or cease.

(6) To protect the anaerobic reactor from nitrate in the effluent and underflow recycle, a new process (the UCT process) is proposed in which the underflow (s) recycle as well as the mixed liquor (a) recycle discharge to the anoxic reactor

*One may ask why not make provision for a Phoredox/UCT/modified UCT process combination by installing the extra recycles. This of course is possible but in converting a Phoredox to a UCT type process, the anaerobic sludge mass fraction immediated is nearly halved (for r=1) and the P removal reduced accordingly.

and an extra (r) recycle is introduced from the anoxic to the anaerobic reactors. By controlling the a-recycle ratio the nitrate concentration in the anoxic reactor can be maintained at near zero so that the r-recycle will contain little or zero nitrate and the rapidly biodegradable COD concentration in the anaerobic reactor is at a maximum level possible. This can be maintained in the process up to influent TKN/COD ratios of about 0,14 mgN/mgCOD (at 12°C to 14°C).

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LIST OF SYMBOLS

A_c = anaerobic capacity (mgN/ℓ influent) i.e. difference between an unaerated reactor's denitrification potential (D_p) and the nitrate entering it.

a = mixed liquor recycle ratio from the aerobic to the anoxic reactors. Subscript o denotes optimum.

b_{hT} = endogenous mass loss rate for heterotrophic organisms at T°C (/d)

= $b_{h20}(1,029)^{(T-20)}$

b_{h20} = the rate at 20°C = 0,24/d.

D_p = denitrification potential (mgN/ℓ influent). Maximum concentration of nitrate an unaerated reactor can remove by denitrification provided sufficient nitrate is available.

d = dissolved oxygen concentration (mgO/ℓ). Subscripts a, r, s and i refer respectively to the concentrations in the a, r and s-recycles and influent.

f = unbiodegradable fraction of active mass

= 0,20 mgVSS/mgVSS.

f_{bs} = fraction of biodegradable influent COD which is rapidly biodegradable.

f_p = phosphorus fraction of the inert MLVSS

= 0,015 mgP/mgVSS.

f_u = unbiodegradable COD fractions of the influent COD. Subscripts p and s refer to particulate and soluble fractions respectively.

f_x = unaerated sludge *mass* fraction. Subscripts a, 1, 3, t and m refer respectively to the anaerobic, primary anoxic, secondary anoxic, total and maximum allowed. Additional subscript v refers to process volume fractions.

K = general parameter for denitrification rate ($mgNO_3$-N/mgVASS/d). Subscripts 1 and 2 refer respectively to the 1st and 2nd rates in the primary anoxic, and 3 to the rate in the secondary anoxic. Additional subscripts T and 20 refer to T°C and 20°C respectively.

N_n = nitrate concentration (mgN/ℓ). Subscripts e, r and s refer respectively to the concentrations in the effluent and r and s-recycles.

n = fraction of total mass of sludge in process passing through the anaerobic reactor per day.

ΔN = system reduction of nitrate ($mgNO_3$-N/ℓ influent).

P_f = excess phosphorus removal propensity factor (mgCOD/ℓ).

P_s = process phosphorus removed in daily sludge wastage (mgP/ℓ influent).

P_v = COD/VSS ratio of the volatile sludge mass

= 1,48 mgCOD/mgVSS.

ΔP_u = Phosphorus removal due to excess uptake (mgP/ℓ influent).

Q = influent flow rate (ℓ/d).

r = mixed liquor recycle ratio from the anoxic to the anaerobic reactors.

R_s = sludge age (d).

R_{so} = maximum sludge age beyond which maximum influent TKN/COD ratio for complete denitrification does not increase.

R_{an} = actual anaerobic retention time (d).

R = nominal retention time (d). Subscripts 1 and 3 refer to primary and secondary anoxic reactors respectively.

S_f = factor of safety for nitrification.

S_{ti} = total influent COD (mgCOD/ℓ).

S_{bi} = biodegradable influent COD (mgCOD/ℓ).

S_{ui} = unbiodegradable influent COD (mgCOD/ℓ)

S_{bsi} = rapidly biodegradable soluble influent COD.

S_{bpi} = slowly biodegradable particulate influent COD.

S_{upi} = particulate unbiodegradable influent COD.

S_{usi} = soluble unbiodegradable influent COD.

S_{bsa} = concentration of rapidly biodegradable COD in the anaerobic reactor (mgCOD/ℓ)

ΔS_{bs} = rapidly biodegradable COD utilized in the anaerobic reactor due to dissolved oxygen and nitrate discharged to it.

t = duration of first denitrification rate in the primary anoxic reactor (h).

T = temperature. Subscripts max. and min. refer respectively to maximum and minimum.

V = volume (ℓ). Subscripts an, ax, ae and t refer respectively to the anaerobic, anoxic and aerobic reactors and the process total.

X = volatile sludge concentration (mgVSS/ℓ). Subscripts an, ax, ae refer to the anaerobic, anoxic and aerobic reactors.

$\bar{X}$ = weighted average volatile sludge concentration in the process (mgVSS/ℓ).

X_a = active mass concentration (mgVASS/ℓ).

Y_h = growth yield coefficient = 0,45 mgVSS/mgCOD.

α = denitrification attributable to the rapidly biodegradable COD ($mgNO_3$-N/mg biodegradable influent COD).

γ = coefficient of excess phosphorus removal (mgP/mgBASS) i.e. the proportion of phosphorus in the active mass.

μ_{nm} = maximum specific growth rate of the nitrifiers. Subscripts T and 20 refer respectively to T°C and 20°C.

REFERENCES

Barnard, J.L. (1973). Biological denitrification. Wat.Pollut.Control, 72, 6, 705-720.

Barnard, J.L. (1974). Cut N and P without chemicals. Water and Wastes Eng., 11, 7, 33-36.

Barnard, J.L. (1975). Nutrient removal in biological systems. Wat.Pollut. Control, 74, 143-154.

Barnard, J.L. (1976). A review of biological phosphorus removal in the activated sludge process. Water S.A., 2, 3, 136-144.

Dold, P.L., G.A.Ekama and G.v.R.Marais (1980). A general model for the activated sludge process. Prog.Wat.Tech., 12, 47-77.

Dold, P.L., H.O.Buhr and G.v.R.Marais (1982). Design and Control of Equalization Tanks. Research Report No. W 42, Department of Civil Engineering, University of Cape Town.

Ekama, G.A. and G.v.R.Marais (1978). The dynamic behaviour of the activated sludge process. Research Report No. W 27, Department of Civil Engineering, University of Cape Town.

Ekama, G.A., A.C.van Haandel and G.v.R.Marais (1979). The present status of research on nitrogen removal : a model for the modified activated sludge process. Presented at the Symposium on Nutrient Removal, S.A. Branch of I.W.P.C. Pretoria, May 1979. Proceedings published by Water Research Commission of South Africa.

Fuh, G.W. and Min Chen (1975). Microbiological basis of phosphate removal in the activated sludge process for the treatment of wastewater. Microbial Ecology, 2, 119-138.

Marais, G.v.R. and G.A. Ekama (1976). The activated sludge process Part I - steady state behaviour. Water S.A., 2, 4, 163-200.

Marsden, M.G. and G.v.R.Marais (1977). The rôle of the primary anoxic reactor in denitrification and biological phosphorus removal. Research Report No. W 19, Department of Civil Engineering, University of Cape Town.

Martin, K.A.C. and G.v.R.Marais (1975). Kinetics of enhanced phosphorus removal in the activated sludge process. Research Report No. W 14, Department of Civil Engineering, University of Cape Town.

McLaren, A.R. and R.J.Wood (1976). Effective phosphorus removal from sewage by biological means. Water S.A., 2, 1, 47-50.

Nicholls, H.A. (1975). Full scale experimentation on the new Johannesburg extended aeration plant. Water S.A., 1, 3, 121-132.

Nicholls, H.A. (1982). Application of the Marais-Ekama activated sludge model to large plants. Presented at 11th IAWPR Conf. Cape Town. Proc. to be published in Water Science and Technology.

Rabinowitz, B. and G.v.R. Marais (1980). Chemical and biological phosphorus removal in the activated sludge process. Research Report No. W 32, Department of Civil Engineering, University of Cape Town.

Siebritz, I.P., G.A.Ekama and G.v.R.Marais (1980). Excess Biological Phosphorus removal in the Activated Sludge Process at Warm Temperate Climates. Proc. Waste Treatment and Utilization, Vol.2, 233-251, Eds. C.W. Robinson, M. Moo-Young and G.J.Farquhar, Pergamon Press, Toronto.

Simpkins, M.J. and R.A.McLaren (1978). Consistent biological phosphate and nitrate removal in an activated sludge plant. Prog.Wat.Tech., 10, 5/6, 433-442.

Stern, L.B. and G.v.R.Marais (1974). Sewage as the electron donor in biological denitrification. Research Report No. W 7, Department of Civil Engineering, University of Cape Town.

van Haandel, A.C., G.A.Ekama and G.v.R.Marais (1981). The activated sludge process Part 3 - single sludge denitrification. Water Research, 15, 1135-1152.

van Haandel, A.C., P.L.Dold and G.v.R.Marais (1982). Optimization of Nitrogen removal in the single sludge activated sludge process. Presented at 11th IAWPR Conf. Cape Town. To be published in Water, Science and Technology.

Wilson, D.E. and G.v.R.Marais (1976). Adsorption phase in biological denitrification. Research Report No. W 11, Department of Civil Engineering, University of Cape Town.

Wat.Sci.Tech., 15, 3/4, 283-318, 1983

CONSIDERATIONS IN THE PROCESS DESIGN OF NUTRIENT REMOVAL ACTIVATED SLUDGE PROCESSES

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Abstract

The average influent wastewater characteristics - (i) the COD concentration, (ii) the TKN/COD concentration ratio, (iii) the rapidly biodegradable COD concentration, (iv) the maximum specific growth rate of the nitrifiers at 20°C attainable in the wastewater, (v) the maximum and minimum temperatures, and (vi) the P/COD concentration ratio - are shown to govern the design of, and effluent quality from single sludge activated sludge processes for both biological nitrogen and phosphorus removal. The TKN/COD ratio governs the selection of the process type: For the Phoredox process, complete denitrification is essential to obtain excess P removal, and this is shown to be feasible only for TKN/COD ratios less than 0,07 to 0,08 mgN/mgCOD; as the TKN/COD ratio increases above 0,08, complete denitrification becomes increasingly unlikely, and the UCT or Modified UCT processes are appropriate because in these processes complete denitrification is not essential to achieve excess P removal - in these processes N and P removal can be traded off against each other depending on the critical nutrient to be removed. Primary sedimentation significantly reduces the biological nutrient removal potential of activated sludge process because it increases the TKN/COD and P/COD ratios and reduces the COD load; however it significantly reduces the process volume and total oxygen demand.

INTRODUCTION

The basic theories describing the behaviour of aerobic COD degradation, nitrification, denitrification and excess biological Phosphorus removal in the single sludge activated sludge process have been set out in a series of 5 papers: 1) Marais and Ekama (1976), 2) Dold, Ekama and Marais (1980), 3) van Haandel, Ekama and Marais (1981), 4) van Haandel, Dold and Marais (1982) and 5) Siebritz, Ekama and Marais (1982). The process design of purely aerobic and nitrification-denitrification processes for nitrogen removal have been dealt with in this series, but not the process design for excess P removal. Design of processes to give N and excess biological P removal, requires an intimate understanding of aerobic and nitrification-denitrification behaviour and continuous reference to the papers above will be made. To avoid repetitive quotation of authors, any unreferenced statements in this paper with regard to N and excess P removal process behaviour must be presumed to have their origin wholly in the above series.

Factors affecting the design of excess P removal processes are

(1) Influent wastewater characteristics: (i) COD concentration, (ii) TKN/COD

concentration ratio, (iii) rapidly biodegradable COD fraction, (iv) maximum specific growth rate of the nitrifiers at 20°C, (v) minimum and maximum temperature and (vi) P/COD concentration ratio. Characteristics (i) to (v) are the same as those required for the design nitrogen removal processes; for excess P removal the P/COD ratio comes into consideration additionally.

(2) Settling characteristics: In order to maintain relatively good sludge settling characteristics in the process, it is necessary that the *actual anoxic* retention time should not exceed about 1 hour.

(3) Effluent required: If upper limits are set to the concentrations of TKN, nitrate and phosphorus allowed in the effluent, the objective in the design is either to satisfy these limits with an appropriate factor of safety, or where the wastewater characteristics are such that it is not possible to satisfy all or any of the limits, to give optimal removal of these concentrations.

The design of a process for simultaneous removal of N and P basically involves the utilization of the influent wastewater characteristics to find (i) an optimal division of the sludge mass in the process into aerated and unaerated fractions to ensure efficient nitrification and (ii) an optimal subdivision of the unaerated fraction into anaerobic (for P removal) and anoxic (for N removal) subfractions to achieve the required, or the best possible, N and P effluent quality.

Consideration will be given first to N removal by consideration of the Bardenpho (Fig 1) and the Modified Ludzack-Ettinger (MLE) (Fig 2) processes; this will facilitate understanding of N removal in the Phoredox (Figs 3 and 4) and UCT type (Figs 5 and 6) processes for, with regard to N removal, these processes are extensions of the Bardenpho and MLE processes respectively. Understanding of the N removal behaviour of the Phoredox and UCT processes is fundamental to the understanding of the P removal behaviour of these processes because N removal has an important influence on the P removal.

The design considerations presented in this paper are restricted to constant flow and load conditions. Constant flow and load conditions allow the use of simple, but accurate design equations to estimate the sludge production per day, sludge mass in the process, process volume, daily average total oxygen demand and division of the total sludge mass in the process into anaerobic, anoxic and aerobic sludge mass fractions for optimal removal of N and P. The design obtained for constant flow and load conditions can then be checked for the expected daily cyclic loading conditions with the aid of the general dynamic activated sludge model.* In most instances it will be found that a design for constant flow and load conditions will be adequate for cyclic flow and load conditions (provided the oxygen supply can be regulated according to the demand). Analysis by means of the general dynamic model however allows the design to be analysed rapidly for a range of different loading conditions and wastewater characteristics to check the adequacy and limitations of the design to possible deviations of wastewater characteristics and loading patterns away from the accepted ones.

On first sight the design theory for denitrification appears to be very different from that presented by van Haandel *et al.* (1982). The difference is apparent, not real. The basic denitrification theory is the same, only the *approach* to design is different: van Haandel *et al.* specify the effluent nitrate concentration in terms of the capability of the Bardenpho or MLE processes and, specifying some of the wastewater characteristics, determine the influent TKN/COD ratio for which the processes can optimally achieve the specified effluent nitrate concentration; in this

*The general activated sludge process model is operational on the computer system (UNIVAC) of the University of Cape Town. The dynamic model can be used only once the process design is completed because the model requires the process configuration, magnitudes of the reactor volumes and recycle ratios to be specified in order to simulate the behaviour for the specified influent wastewater characteristics under daily cyclic loading conditions.

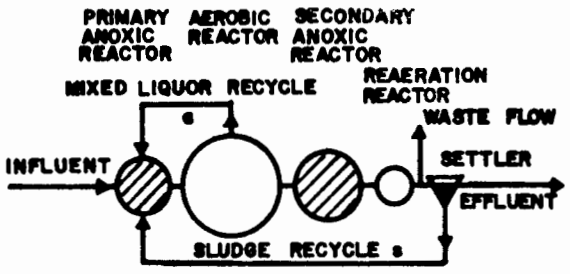

Fig 1 The Bardenpho process for biological nitrogen removal

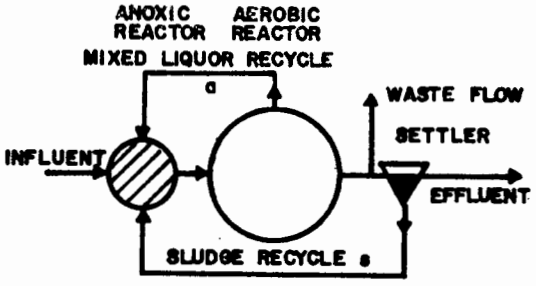

Fig 2 The modified Ludzack-Ettinger process for biological nitrogen removal

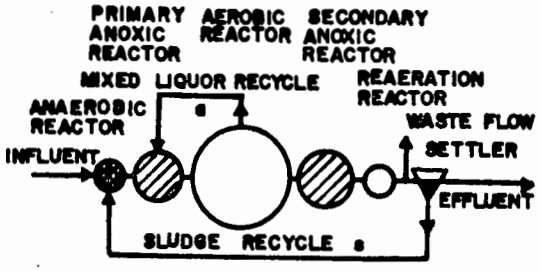

Fig 3 The Phoredox process for biological nitrogen and phosphorus removal

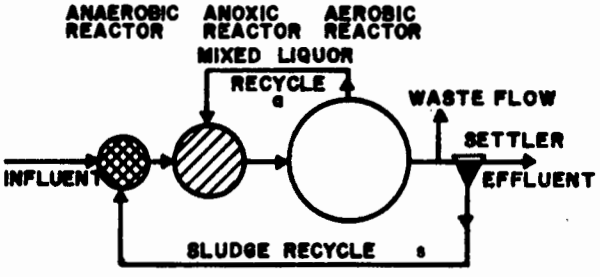

Fig 4 The modified Phoredox process for biological nitrogen and phosphorus removal

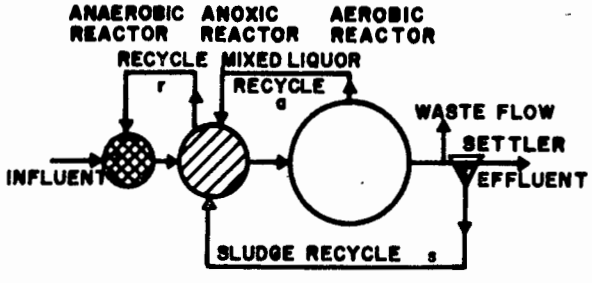

Fig 5 The UCT process for biological nitrogen and phosphorus removal

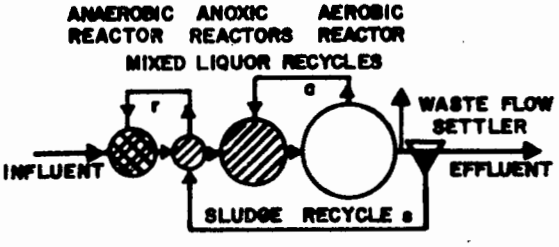

Fig 6 The modified UCT process for biological nitrogen and phosphorus removal

paper all the wastewater characteristics are specified including the TKN/COD ratio and the best process type for optimal N removal is determined. This latter approach, although more laborious in that it may require a trial and error procedure, has the advantage that it readily incorporates the additional variable of the subdivision of the unaerated sludge mass fractions into anaerobic and anoxic fractions for optimal P and N removal. Also the effect of dissolved oxygen in the recycle flows is readily incorporated.

MAXIMUM UNAERATED SLUDGE MASS FRACTION AND ITS INFLUENCE ON SLUDGE AGE

In biological treatment of municipal wasteflows, nitrification is a prerequisite for N removal by denitrification. Nitrification, being mediated by the obligate aerobic organisms *Nitrosomonas* and *Nitrobacter*, can take place only if the *aerobic* sludge age of the process is sufficiently long to allow growth of these organisms. Consequently for a selected *process* sludge age, the maximum fraction of the total sludge mass under *unaerated* conditions is limited to that value which maintains the aerobic sludge age above a minimum value. Because the rate of growth of the nitrifiers decreases with decrease in temperature, the minimum aerobic sludge age is fixed by the minimum expected wastewater temperature. The denitrification potential of the process depends *inter alia* on the *unaerated* sludge mass fraction; if too small, all the nitrate produced by nitrification cannot be removed. Consequently it may be necessary to increase the *process* sludge age in order to increase the unaerated sludge mass fraction, while maintaining the required minimum aerobic

sludge age. When excess biological P removal is incorporated in the process design, a fraction of the unaerated sludge mass must be reserved to establish the required anaerobic conditions i.e. the unaerated sludge mass fraction now consists of two fractions, anoxic and anaerobic. The anaerobic fraction in a correctly designed plant will not receive any nitrate and hence does not contribute towards the denitrification potential of the process. Consequently, for some fixed minimum aerobic sludge age to achieve nitrification, the process sludge age for both P and N removal will be even longer than that for N removal only, to allow the establishment of the required anaerobic conditions and denitrification.

Calculation of the Maximum Unaerated Sludge Mass Fraction

The maximum unaerated sludge mass fraction (f_{xm}) that will allow nitrification just to take place at a sludge age of R_s, is given by van Haandel *et al.*(1982) as

$$f_{xm} = 1 - (b_{nT} + 1/R_s)/\mu_{nmT} \qquad (1a)$$

The corresponding aerobic sludge mass fraction is given by $(1-f_{xm})$ i.e.

$$(1-f_{xm}) = (b_{nT} + 1/R_s)/\mu_{nmT} \qquad (1b)$$

TABLE 1 Temperature Dependency of Nitrification Constants

Parameter	Symbol	Temperature Dependency Equation	θ	Reference Value (20°)
Maximum Specific growth rate (/d)	μ_{nm}	$\mu_{nmT} = \mu_{nm20}\theta^{(T-20)}$	1,123	0,20 to 0,65
Endogenous mass loss rate (/d)	b_n	$b_{nT} = b_{n20}\theta^{(T-20)}$	1,029	0,04
Note: Additional subscripts T or 20 refer to values at T or 20°C respectively				

The temperature dependencies of b_{nT} and μ_{nmT} are given in Table 1. Using the data in Table 1, a diagrammatic representation of Eq(1) is given in Fig 7 for μ_{nm20} = 0,65 and 0,33/d respectively. The diagram shows that f_{xm} is very sensitive to μ_{nmT}: unless a sufficiently large aerobic sludge mass fraction $(1-f_{xm})$ is provided, (see right hand side of Fig 7), nitrification will not take place and no nitrogen removal by denitrification is possible.

The design value of $(1-f_{xm})$ always should be significantly higher than that given by Eq(1b) because nitrification becomes unstable as the unaerated sludge mass fraction approaches (f_{xm}) from a lower value, particularly under cyclic loading conditions. Consequently to ensure efficient nitrification (>95%) it is recommended that the minimum *aerobic sludge mass fraction* $(1-f_{xm})$ is increased by a safety factor (S_f) of about 1,25 to 1,50. Hence Eq(1b) becomes

$$(1-f_{xm}) = S_f\,(b_{nT} + 1/R_s)/\mu_{nmT} \qquad (2)$$

For a selected μ_{nm20} value and a factor of safety (S_f) of say 1,3, the maximum unaerated sludge mass fraction (f_{xm}) for a selected sludge (R_s) is governed by the *lowest expected temperature* (Eq 2). Having fixed f_{xm} for the lowest expected temperature and the selected sludge age, an increase in temperature always results in an increased factor of safety (S_f) and a decrease in effluent TKN concentration, i.e. an increase in temperature increases the certainty and efficiency of nitrification.

Estimation of the Maximum Specific Growth Rate of the Nitrifiers at 20°C

In the determination of f_{xm}, the principal problem lies in the selection of the

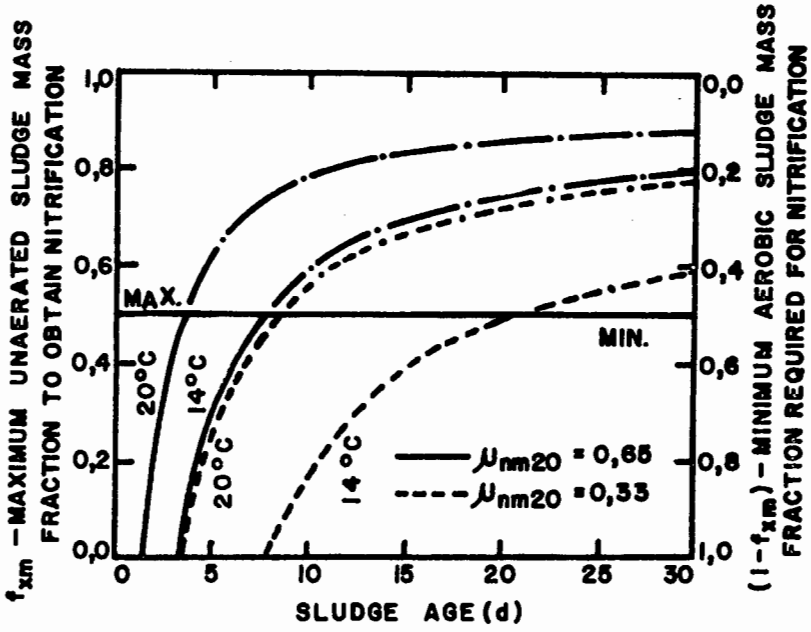

Fig 7 Maximum permissible unaerated sludge mass fraction (f_{xm}) or minimum aerobic sludge mass fraction ($1-f_{xm}$) required to just sustain nitrification versus sludge age at 20°C and 14°C for different maximum specific growth rates of the nitrifiers at 20°C (μ_{nm20})

maximum specific growth rate of the nitrifiers at 20°C* (μ_{nm20}) as the magnitude of this constant has a significant effect on the magnitude of f_{xm}. The magnitude of μ_{nm20} tends to be specific for a specific wastewater source; this behaviour is so evident that μ_{nm20} should be considered a wastewater characteristic. In a purely domestic wastewater, a high value for μ_{nm20} of about 0,65/d is not unusual but the presence of an industrial fraction or toxic substance in the influent flow can suppress the value to below 0,30/d. Furthermore μ_{nm20} is sharply reduced at pH values below 7,0; the reduction of the Alkalinity to low values in nitrification-denitrification plants treating wastewaters with low Alkalinities (<200 mg/ℓ as $CaCO_3$),can cause the mixed liquor pH to fall below 7 with a concomitant reduction in the μ_{nm20} value. This is illustrated in Fig 8 which shows the interrelationship between mixed liquor Alkalinity and pH for different concentrations of dissolved CO_2.

In the course of nitrification 1 mg(NH_4^+-N) converted to 1 mg(NO_3^--N) absorbs 7,14 mg Alkalinity and in denitrification 1 mg(NO_3^--N) converted to 1 mg(N_2-N) gas produces 3,57 mg/ℓ Alkalinity as $CaCO_3$; if the mixed liquor Alkalinity is reduced below about 50 mg/ℓ as $CaCO_3$, then from Fig 8, it can be seen that a significant decrease in pH below 7,0 can take place, with a concomitant reduction in the μ_{nm20} value.

Ideally the μ_{nm20} value should be, and can be measured by experiment (van Haandel and Marais, 1981 and Sehayek and Marais, 1981) but in the absence of information on μ_{nm20} a low value necessarily must be selected, say 0,35/d, to have reasonable assurance of a safe design with respect to nitrification. However, using a low value when the actual value is higher, reduces the optimal design of the process in that it forces the selection of a long sludge age (about 25 days) for a reasonable design value of f_{xm} of 0,45 (Eq 2).

Tc obtain complete removals of N in P removal processes the unaerated sludge mass fraction f_{xm} usually must be high. If the μ_{nm20} values are low, i.e. <0,40/d (which will be the usual case in design where insufficient information on the μ_{nm20} value is available) the necessary f_{xm} values are obtained only at long sludge ages e.g. if μ_{nm20} = 0,35/d then with S_f = 1,3 and T_{min} = 14°C, a sludge age of 25 days

*The value of the maximum specific growth rate of the nitrifiers at 20°C (μ_{nm20}) is the reference value; knowing the rate at 20°C, the rates at other temperatures from 12°C to 26°C can be calculated from the equation in Table 1.

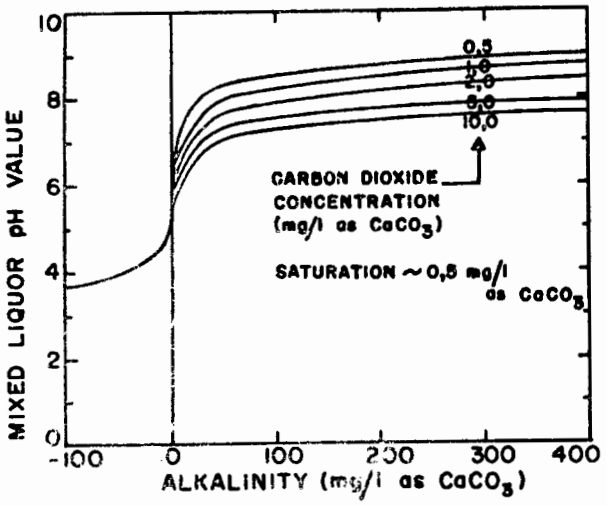

Fig 8 Interrelationship between Alkalinity, pH and CO_2 concentration

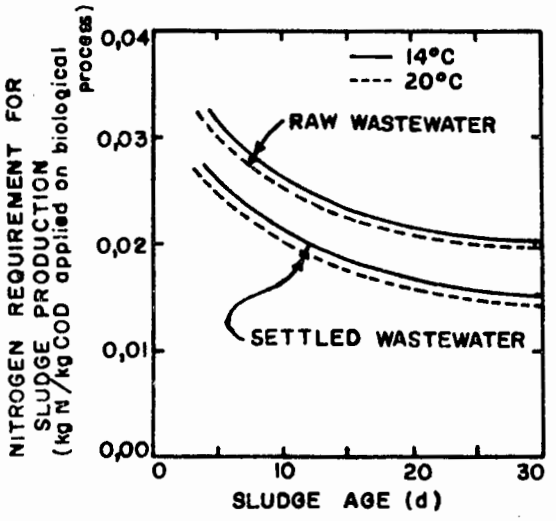

Fig 9 Nitrogen requirement for sludge production per kg COD load on the biological process versus sludge age for raw and settled wastewaters at 14°C and 20°C

is required for an f_{xm} = 0,45 and 35 days for an f_{xm} of 0,54. However, long sludge ages require large process volumes - increasing the sludge age from 25 to 35 days increases the process volume by about 33% (Fig 16) whereas the unaerated sludge mass fraction increases only 20%. Consequently, for low μ_{nm20} values, the increase in N and P removal that can be obtained by increasing f_{xm} above 0,50 may not be economical due to the large process volumes this requires. This imposes an upper limit to f_{xm} near 0,50 to avoid the excessively large process volumes required at very long sludge ages*.

THE EFFECT OF THE INFLUENT TKN/COD RATIO ON THE SELECTION OF THE PROCESS TYPE

For a given wastewater and process configuration, if the sludge age, unaerated sludge mass fraction and its subdivision into anoxic and anaerobic fractions are fixed, the *removals* of N and P per unit influent COD also are fixed. Hence, for a given design and wastewater the *effluent* N and P concentrations depend on the influent TKN/COD and P/COD ratios. The fact that for a given design and wastewater the removals of N and P are fixed, implies that there are limits to the TKN/COD and P/COD with which complete N and P removal can be achieved in biological nutrient removal processes; however, the limits are different for the various N and P removal processes. The recognition of these limits, in particular that associated with N removal, is of prime importance in nutrient removal process type selection.

*Additional information on the need for an upper limit to f_{xm} comes from experimental work on the Ludzack-Ettinger process and theoretical predictions using the general activated sludge model. At 20°C with R_S = 20 days, if f_{xm} >0,70, the mass of sludge generated increases sharply, an observation also indicated by theoretical simulation: theoretically, this happens for f_{xm} >0,60 at T = 14°C and R_S = 20 days. The reason is that for such high f_{xm}, the exposure of the sludge to aerobic conditions becomes insufficient to utilize the adsorbed and enmeshed particulate material. This leads to a decrease in active mass and oxygen demand and a build-up of enmeshed material, which causes a progressive decline in process activity because of the decline in active mass. When this happens, the process still *functions* in that the COD is removed from the wastewater, but the degradation of the COD is reduced; the process begins to assume the role of a contact reactor of a contact-stabilization process, i.e. a bioflocculator with minimal degradation. This critical state occurs at lower f_{xm} as the temperature is decreased and the sludge age is reduced (Arkley and Marais, 1982).

The Phoredox Process

The configuration of the Phoredox process (Fig 3) is such that the attainment of complete denitrification is of the utmost importance for obtaining excess P removal: If complete denitrification cannot be achieved, nitrate will be present in the effluent and sludge underflow recycle; the discharge of the nitrate present in the underflow recycle to the anaerobic reactor causes a severe deterioration in the excess P removal (Fig 12). For successful excess P removal in the Phoredox process, it must be operated at a sludge age which ensures complete denitrification.

Roughly speaking, if the influent TKN/COD ratio is low (<0,07 mgN/mgCOD) complete denitrification, and hence complete N removal, can be obtained in the Phoredox process with a relatively low anoxic sludge mass fraction (f_{xdm}) i.e. about 0,30. An f_{xdm} = 0,30 and an anaerobic sludge mass fraction (f_{xa}) of say 0,10, gives an unaerated sludge mass fraction of 0,40 which, with a low μ_{nm20} (~0,35/d) requires a sludge age of 20 to 25 days to ensure nitrification with S_f = 1,3. These relatively short sludge ages will allow good P removal per unit influent COD (Fig 11). At slightly higher TKN/COD ratios (~0,08 mgN/mgCOD) a larger anoxic sludge mass fraction (f_{xdm}) is required to obtain complete denitrification (~0,45) which when combined with an anaerobic sludge mass fraction (f_{xa}) of 0,10 to give an unaerated sludge mass fraction of 0,55 results in sludge ages of around 35 days at low μ_{nm20} values. At these very long sludge ages, the P removal per unit influent COD is low (Fig 11). Consequently for TKN/COD ratios equal or less than 0,07 mgN/mgCOD, complete denitrification is attainable, and the Phoredox process may be a viable option for N and P removal*. However, for TKN/COD ratios near 0,08 mgN/mgCOD, the sludge age will be very long requiring large process volumes per unit influent COD (Fig 16) and give relatively low P removals per unit influent COD (Fig 11), i.e. at TKN/COD ratios of 0,08, the process no longer may be economically viable.

It can be concluded from the above discussion that, because complete denitrification is required to obtain excess P removal in the Phoredox process, the process rapidly becomes unrealistic for TKN/COD ratios near 0,08 mgN/mgCOD, requiring unaerated sludge mass fractions greater than 0,50 and sludge ages longer than 35 days. For the TKN/COD ratio above 0,08 mgN/mgCOD, the achievement of complete denitrification is untenable, and the presence of nitrate in the effluent and underflow recycle is inevitable, so that for TKN/COD above 0,08, the Phoredox process no longer is a viable option.

The upper limit of the TKN/COD ratio of 0,07 to 0,08 mgN/mgCOD for successful operation of the Phoredox process severely restricts application of the process in the treatment of municipal wastewaters because the TKN/COD ratios for raw wastewaters range between 0,07 to 0,08 mgN/mgCOD and for settled wastewaters generally are greater than 0,10 mgN/mgCOD. A further difficulty with this process is that it is inflexible to accommodate TKN/COD ratios higher than that for which the process is designed. Once the ratio increases above the accepted design value, the effluent nitrate concentration increases concomitantly leading to a decline in excess P removal (Fig 12). The only operational flexibility of the process to reduce the nitrate discharge to the anaerobic reactor is the reduction of the underflow recycle ratio but this may result in failure of the secondary settling tank.

The UCT Type Processes

If the TKN/COD ratio is greater than 0,08 mgN/mgCOD, the only viable processes for obtaining excess P removal are the UCT and modified UCT processes (Figs 5 and 6). In these processes complete denitrification is not essential for obtaining excess P removal because nitrate is positively excluded from the anaerobic reactor by means of the mixed liquor and sludge recycle arrangement and their appropriate control: In the UCT process for example, the sludge underflow s-recycle is

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*The modified Phoredox process (Fig 4) is never a viable alternative as nitrate will always be present in the effluent and cannot be positively excluded from the anaerobic reactor. Owing to this deficiency, this process will not be considered further in this paper.

discharged to the anoxic reactor and an additional mixed liquor r-recycle from the anoxic to the anaerobic reactor is introduced. The nitrate recycled to the anoxic reactor can be controlled by appropriately adjusting the mixed liquor a-recycle from the aerobic to the anoxic reactor such that the nitrate concentration in the anoxic reactor is approximately zero. Hence, nitrate discharge to the anaerobic reactor via the r-recycle can be avoided and optimal anaerobic conditions can be maintained for excess P removal.

The UCT process has flexibility to accommodate higher TKN/COD ratios than that accepted in its design without jeopardizing the achievement of excess P removal. This is done simply by reducing the mixed liquor a-recycle ratio until the nitrate concentration again is zero in the anoxic reactor. The UCT process can be designed (and operated) to deal with mean TKN/COD ratios up to 0,14 mgN/mgCOD. At a TKN/COD ratio of 0,14, the nitrate concentration in the s-recycle ratio is so high that this nitrate load on the anoxic reactor is sufficient to load it to its denitrification potential and the a-recycle ratio reduces to zero. Once the a-recycle ratio is zero any increase in TKN/COD ratio will cause a nitrate discharge to the anaerobic reactor. Hence, at TKN/COD ratios above 0,14 mgN/mgCOD, the UCT process cannot be designed to achieve excess P removal. However this value is above that of most raw and settled municipal wastewaters.

Experience with the UCT process brought to light a different type of problem that can result in failure of the process. In this process, as the TKN/COD ratio increases, the a-recycle ratio needs to be reduced to avoid overloading the anoxic reactor with nitrate which may cause a nitrate discharge to the anaerobic reactor. However, a reduction in the a-recycle ratio causes an increase in the *actual anoxic* retention time. It was found that generally for high influent COD concentrations (>500 mgCOD/ℓ) and TKN/COD ratios >0,11 mgN/mgCOD, the actual anoxic retention times are longer than 1 hour. From experimental results, there are strong indications that when the actual anoxic retention time increases to longer than 1 hour, the settleability of the mixed liquor sharply declines.* The situation therefore arises that the process operates satisfactorily with regard to P removal, but may fail due to settleability problems, or if the secondary settling tanks are designed to cope with the poor settling sludge, inordinately large settling tanks will be required. Consequently, in design, to preserve good settleability of the sludge, an upper limit of 1 hour must be imposed on the actual anoxic retention time. This limitation creates a conflict between good P removal and good sludge settleability at TKN/COD ratios >0,10 to 0,11 mgN/mgCOD (depending on the COD strength of the wastewater) because the former demands a low a-recycle ratio and the latter a high one. This conflict was resolved by making a modification to the UCT process.

In the Modified UCT process (Fig 6), the anoxic sludge mass fraction (f_{xdm}) is subdivided into two parts, the first having a sludge mass fraction of 0,10 to 0,12 (depending on the influent COD concentration) and the second having the balance of the f_{xdm}. The first reactor receives the underflow s-recycle and the r-recycle to the anaerobic reactor is taken from it. The second anoxic reactor receives the a-recycle from the aerobic reactor. Because the second anoxic reactor is separated from the first, the a-recycle ratio can have any reasonable value greater than the minimum necessary to fully load the second anoxic reactor to its denitrification potential. The a-recycle ratio can therefore be set at the greater of two lower limits i.e. set sufficiently high to (i) load the second anoxic reactor to its denitrification potential or (ii) maintain an actual anoxic retention time of less than 1 hour. If the ratio given by limit (ii) is greater than that given by limit (i) the second anoxic reactor will have a nitrate load greater than its denitrification potential - this will not greatly affect its N removal efficiency provided the D.O. concentration in the a-recycle is below 2 to 3 mgO/ℓ. An important operational advantage of the Modified UCT process over the UCT process is

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*For reasons not yet understood, the anaerobic retention time, both nominal and actual, does not appear to affect the settleability of the sludge.

that it obviates the need for careful control of the a-recycle ratio to ensure a nitrate free discharge to the anaerobic reactor. However, this advantage is at a cost: the process is unlikely to operate satisfactorily with respect to excess P removal for TKN/COD ratios above 0,11 mgN/mgCOD.

In the UCT and modified UCT processes, by varying the subdivision of the unaerated sludge mass fraction, f_{xm}, between the anaerobic, f_{xa}, and anoxic, f_{xdm}, sludge mass fractions, good N or P removal can be traded off against each other depending on the critical nutrient to be removed. For example if the μ_{nm20} value is low, short sludge ages (R_s) and large anaerobic sludge mass fractions (f_{xa}) can be combined to achieve nitrification and high P removal per unit influent COD, but because a short R_s and large f_{xa} restrict the anoxic sludge mass fraction (f_{xdm}) to a relatively low value, the nitrate removal per unit influent COD will be poor.

The discussion above qualitatively illustrated the importance of the TKN/COD ratio on biological N and P removal and the selection of the process type. Quantitative procedures to calculate the magnitude of the N and P removal from the influent wastewater characteristics will now be discussed.

PRINCIPLES OF NITROGEN REMOVAL

Understanding of N removal in the activated sludge process is facilitated by defining two parameters, i.e. nitrification capacity and denitrification potential.

(1) Nitrification capacity

Not all the influent TKN is available for nitrification: some is required for daily sludge production and some escapes with the effluent. Hence the TKN concentration per litre influent *available* for nitrification i.e. the nitrification capacity (N_c), is given by the difference between the influent TKN concentration (N_{ti}) and the sum of the effluent TKN concentration (N_{te}) and the nitrogen required for nett sludge production (N_s), i.e.

$$N_c = N_{ti} - N_s - N_{te} \qquad (3)$$

The nitrogen required for sludge production (N_s) is given by Marais and Ekama (1976) as:

$$N_s = S_{ti}\left\{\frac{Y_h(1 - f_{us} - f_{up})(1 + fb_{hT}R_s)}{(1 + b_{hT}R_s)} + \frac{f_{up}}{P_v}\right\} f_n \qquad (4)$$

A plot of N_s/S_{ti} (Eq 4 divided by S_{ti}) versus sludge age (R_s) is given in Fig 9 for 14°C and 20°C for the raw and settled municipal wastewater characteristics taken from Table 2*.

The effluent TKN concentration (N_{te}) depends on the efficiency with which the TKN is converted to nitrate. If the safety factor (S_f) with which f_{xm} is calculated (Eq 2) is selected greater than about 1,3 at the *lowest expected process temperature* (T_{min}) the efficiency of nitrification will be high (>95%) and N_{te} generally will be less than 4mgN/ℓ and independent of both the process configuration and the sludge mass subdivision into aerated and unaerated fractions (provided sufficient aeration capacity is available). Hence, provided $S_f \geq 1,3$ at T_{min}, usually N_{te} need not be calculated explicitly** and can be taken to be approximately 4 mgN/ℓ. For the selected f_{xm}, sludge age (R_s) and T_{min}, an increase in temperature will increase the nitrification efficiency and also the factor of safety (S_f) so that at summer temperatures (T_{max}), N_{te} will be lower (i.e. about 2 mgN/ℓ) than during the winter temperatures.

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*The characteristics of the raw and settled wastewaters given in Table 2 are approximately normal for municipal raw and settled wastewaters and will be utilized throughout this paper to demonstrate the design of nutrient removal plants.

**Explicit equations for the effluent TKN concentration i.e. the sum of the effluent ammonia and organic nitrogen concentrations, are given by van Haandel *et al.* (1982).

TABLE 2 Assumed Raw and Settled Municipal Wastewater Characteristics for a raw wastewater COD of 600 mgCOD/ℓ

Parameter	Symbol	Units	Raw	Settled*
Total COD	S_{ti}	mgCOD/ℓ	600**	360
Total TKN	N_{ti}	mgN/ℓ	48	41
Total P	P_{ti}	mgP/ℓ	10	8,5
Rapidly biodegradable COD fraction	f_{bs}	mgCOD/mgCOD	0,24	0,33
TKN/COD ratio		mgN/mgCOD	0,08	0,114
P/COD ratio		mgP/mgCOD	0,017	0,024
Unbiodegradable fractions:				
(i) Particulate	f_{up}	mgCOD/mgCOD	0,13	0,04
(ii) Soluble	f_{us}	mgCOD/mgCOD	0,05	0,08
Maximum Specific Growth Rate of Nitrifiers at 20°C	μ_{nm20}	/d	0,36	0,36
Temperature:	T_{max}	°C	20	20
	T_{min}	°C	14	14

*Primary sedimentation is assumed to remove 40% COD, 15% TKN, 15% P and 10% of the rapidly biodegradable COD. The fractions and ratios for the settled sewage are based on the settled sewage COD.

**At raw wastewater COD concentrations other than 600 mgCOD/ℓ, the concentrations of the other constituents generally change proportionately.

Knowing N_s from Eq (4) for the selected sludge age (R_s) and temperature (T), and taking N_{te} to be between 2 to 4 mgN/ℓ depending on the temperature, the nitrification capacity (N_c) can be calculated from Eq (3). Because N_{te} and N_s are independent of f_{xm} (provided S_f >1,3), N_c also is independent of f_{xm}. However, because N_s is a function of R_s and T (Fig 9) and N_{te} a function of T, N_c also is a function of R_s and T, and increases with increase in R_s or T.

(2) Denitrification potential

The denitrification potential (D_p) of a reactor under constant flow and load conditions is defined as the concentration of nitrate per unit influent flow that the reactor can denitrify if sufficient nitrate is always present (van Haandel *et al.* 1982). They showed that the denitrification potential for a primary anoxic reactor (D_{p1}) is given by

$$D_{p1} = (1 - f_{us} - f_{up})S_{ti}\{\underbrace{\frac{f_{bs}(1 - P_v Y_h)}{2,86}}_{(A)} + \underbrace{\frac{Y_h R_s}{(1 + b_{hT}R_s)}}_{(B)} K_{2T} f_{x1}\} \quad (5)$$

and for a secondary anoxic reactor (D_{p3}) is given by

$$D_{p3} = (1 - f_{us} - f_{up})S_{ti}\{\underbrace{\frac{Y_h R_s}{(1 + b_{hT}R_s)}}_{(C)} K_{3T} f_{x3}\} \quad (6)$$

where

K_{2T} = the second denitrification rate at T°C in the primary anoxic reactor ($mgNO_3$-N/mgVASS/d)

$= K_{220}(1,08)^{(T-20)}$ for $T > 13°C$; $K_{2T} = K_{3T}$ for $T < 13°C$ (7)

K_{220} = 0,1008 mg(NO_3-N)/mgVASS/d (van Haandel *et al.* 1981).

K_{3T} = the denitrification rate in the secondary anoxic reactor at T°C (mgNO_3-N/mgVASS/d)

$= K_{320}(1,029)^{(T-20)}$ (8)

K_{320} = 0,072 mg(NO_3-N)/mgVASS/d (van Haandel *et al.* 1981).

Term (A) in Eq (5) is the denitrification attributable to the utilization of the influent rapidly biodegradable COD fraction, f_{bs}. Equation (5) is based on the assumption that this fraction is completely utilized in the primary anoxic reactor. For this to be true f_{x1} must be greater than f_{x1min}, where

$$f_{x1min} = f_{bs}(1-P_v Y_h)(1+b_{hT} R_s)/(2,86\ K_{1T}\ Y_h\ R_s) \quad (9)$$

where

K_{1T} = rate of denitrification by utilization of rapidly biodegradable COD at T°C (mgNO_3-N/mgVASS/d)

$= K_{120}(1,20)^{(T-20)}$ (10)

K_{120} = 0,720 mgNO_3-N/mgVASS/d (van Haandel *et al.* 1981).

Substituting the values of the kinetic constants P_v, Y_h, b_{hT} and K_{1T} (see List of Symbols), then for f_{bs} = 0,33, f_{x1min} is less than 0,10 for R_s >15 days at 14°C. This value is much lower than for most primary anoxic sludge mass fractions utilized in design, (where f_{x1} usually is greater than 0,15), so that Eq (5) is valid for most design situations (van Haandel *et al.* 1982).

For the raw wastewater characteristics given in Table 2, the denitrification potential per unit influent COD of the primary and secondary anoxic reactors (i.e. D_{p1}/S_{ti} and D_{p3}/S_{ti}) are shown plotted versus sludge age for different unaerated sludge mass fractions at 14°C and 20°C in Fig 10. The plots show that both D_{p1}/S_{ti} and D_{p3}/S_{ti}, (i) increase as R_s increases, but for R_s >20 days the increase is very small and, (ii) both increase markedly with increasing unaerated sludge mass fraction, and (iii), D_{p1} is greater and more sensitive to temperature than D_{p3}.

Similar curves to Fig 10 can be constructed for settled wastewater. Such plots will show that for settled wastewater D_{p1}/S_{ti} is greater than that for raw wastewater but that D_{p3}/S_{ti} remains approximately the same. The increase in D_{p1}/S_{ti} for settled wastewater is because the rapidly biodegradable COD concentration with respect to the total settled biodegradable COD concentration (f_{bs}) increases - primary sedimentation removes mainly particulate and very little soluble COD (see Table 2). However, the absolute magnitude of the denitrification potentials D_{p1} and D_{p3} for settled wastewater are significantly reduced compared to raw wastewater because primary sedimentation significantly reduces the COD load of the wasteflow.

From the definition above, it is evident that the denitrification potential of an anoxic reactor is the *maximum* concentration of nitrate that can be removed by it. If the potential of the reactor is greater than the nitrate load discharged to it, the nitrate concentration in its outflow will be zero but its denitrification *performance* is less than its denitrification potential. If its potential is less than the nitrate discharged to it, nitrate will be present in the outflow and its denitrification performance is equal to its denitrification potential. Once the anoxic reactors of a fixed configuration are loaded with nitrate to their respective denitrification potentials more nitrate cannot be removed by increasing the recycle ratios, i.e. the maximum denitrification performance of a process is limited by its denitrification potential.

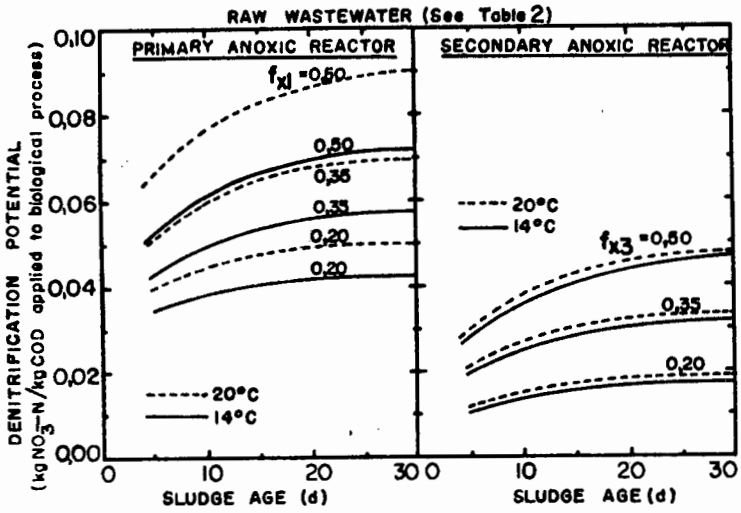

Fig 10 Denitrification potential per kgCOD applied to biological process versus sludge age for primary and secondary anoxic reactors of different unaerated sludge mass fractions (f_{x1} and f_{x3}) for raw wastewater at 14°C and 20°C

PRINCIPLES OF EXCESS BIOLOGICAL PHOSPHORUS REMOVAL

A quantitative parametric model for excess biological P removal in Phoredox and UCT Type nutrient removal processes has been presented by Siebritz *et al.* (1982). In this model two parameters are defined i.e. (i) the coefficient of excess P removal and (ii) the excess P removal propensity factor.

(1) Coefficient of Excess P removal (γ)

Excess P removal is hypothesized to be biologically mediated (Marais, Siebritz and Ekama, 1982). From this hypothesis it follows that (i) the mass of P taken up in excess depends on the mass of P taken up by the active mass in the process and (ii) the magnitude of the removal will depend on the mass of sludge per unit influent COD wasted per day and the fractional content of P in the active, endogenous and inert volatile sludge fractions. Assuming that the magnitude of the fractional content of P in the volatile sludge fractions is γ for the active mass and f_p for the endogenous and inert masses respectively, Martin and Marais (1975) showed that the P removal from the influent, P_s, can be expressed by:

$$Q.P_s = V_p\,(\gamma X_a + f_p X_e + f_p X_i)/R_s$$

$$P_s = (\gamma X_a + f_p X_e + f_p X_i) R_{hn}/R_s$$

$$= S_{ti}\{\frac{(1-f_{us}-f_{up})Y_h}{(1+b_{hT}R_s)}\,(\gamma + f_p f b_{hT} R_s) + f_p\,\frac{f_{up}}{P_v}\} \qquad (11)$$

When biological excess P removal takes place, this will be reflected in the value of γ in Eq (11), the value being greater than the 0,02 to 0,03 mgP/mgVASS usually found for purely aerobic processes. With excess P uptake, γ can range from a minimum of about 0,06 when anoxic conditions only are present, to a maximum of about 0,35 when the appropriate anaerobic conditions are present.

A plot of Eq (11) (divided through by S_{ti}) versus R_s is given in Fig.11 for raw and settled sewage at 14°C and 20°C assuming a constant γ value of 0,18 mgP/mgVASS, a value readily attained in optimally designed P removal plants. Figure 11 shows that P_s/S_{ti} decreases sharply with sludge age so that *to remove the maximum P, the sludge age should be kept as low as possible.* The P removal per unit COD load is approximately the same for raw and settled sewage. Hence, because primary sedimentation removes as much as 40% of the COD load, P removal with settled wastewater is about 40% less than with raw wastewater. For a constant γ the effect of temperature on P removal is small because the nett mass of sludge produced does not

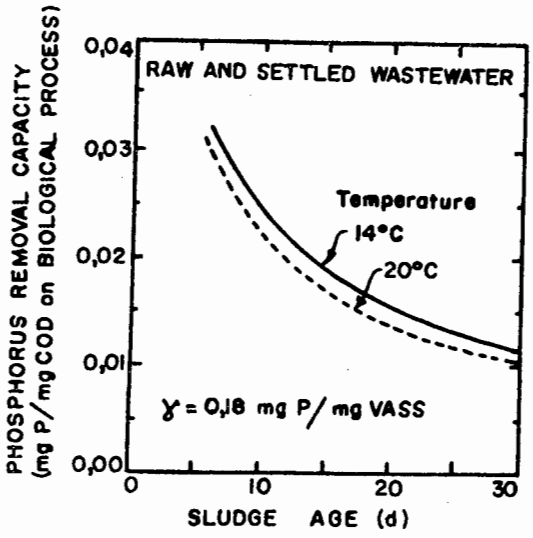

Fig 11 Phosphorus removal per kg COD load on biological process versus sludge age for an excess P removal coefficient (γ) of 0,18 mgP/mgVASS at 14°C and 20°C for raw and settled wastewaters

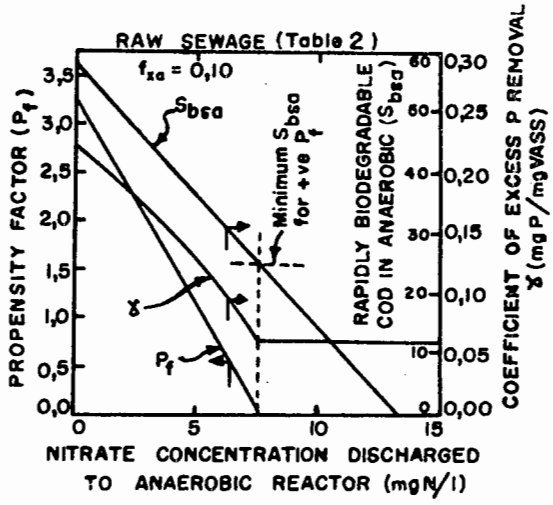

Fig 12 Propensity factor (P_f), rapidly biodegradable COD concentration in anaerobic reactor (S_{bsa}) and coefficient of excess P removal (γ) versus the nitrate concentration discharged to the anaerobic reactor for an anaerobic sludge mass fraction (f_{xa}) of 0,10 for raw wastewater

change significantly with temperature.

(2) Excess P Removal Propensity Factor (P_f)

Siebritz *et al.* (1982) found that the magnitude of the coefficient of excess P removal γ is influenced by a set of conditions in the anaerobic reactor: (i) the magnitude of the rapidly biodegradable COD concentration (S_{bsa}) in excess of 25 mg COD/ℓ, (ii) the actual retention time in the anaerobic reactor and (iii) the mass of sludge (expressed as a fraction of the mass of sludge in the process) passing through the anaerobic reactor each day. These conditions were quantified for the Phoredox and UCT type process and formalized into a parameter called the excess P removal propensity factor, P_f, i.e.

$$P_f = (S_{bsa}-25).f_{xa}; \text{ when } S_{bsa} < 25,\ P_f = 0,0 \quad (12)$$

where

f_{xa} = anaerobic sludge mass fraction

S_{bsa} = rapidly biodegradable COD concentration in the anaerobic reactor (mgCOD/ℓ)

$$= (f_{bs}S_{bi} - \Delta S_{bs})/(1+s \text{ or } r) \quad (13a)$$

where

ΔS_{bs} = rapidly biodegradable COD utilized in the anaerobic reactor

$$= s(N_{ns}.2,86+d_s)/(1-P_vY_h) \text{ for the Phoredox process} \quad (13b)$$

$$= r(N_{nr}.2,86+d_r)/(1-P_vY_h) \text{ for UCT processes} \quad (13c)$$

(3) Excess P Removal Model

From plots of experimentally measured γ and P_f data pairs, these two parameters were linked in the following empirical equation:

$$\gamma = 0,35-0,29 \exp(-0,242\ P_f) \quad (14)$$

Equation (14) shows that the higher the P_f factor, the greater the γ coefficient.

Consequently, at a fixed sludge age, the higher the P_f factor in a process, the greater the P removal per unit COD load. For a fixed f_{xa}, high P_f factors are obtained with (i) high influent COD concentrations (S_{ti}), (ii) high rapidly biodegradable COD fractions (f_{bs}) and (iii) zero nitrate concentrations in the recycles to the anaerobic reactor (N_{ns},N_{nr}). The sensitivity of excess P removal to nitrate discharged to the anaerobic reactor is demonstrated in Fig 12. In Fig 12 the S_{bsa} concentration, P_f factor and γ coefficient calculated from Eqs (11-14) for the raw wastewater given in Table 2 are plotted versus the nitrate concentration discharged to the anaerobic reactor (N_{ns}) for f_{xa} = 0,10 and d_s = 1,0 mgO/ℓ. It can be seen that for N_{ne} >7 mgN/ℓ, the γ coefficient is reduced to a third of that for N_{ns} = 0,0. For R_s = 25 days and T = 14°C this reduction in γ results in a decline in P removal from 9,3 to 3,5 mgP/ℓ. This example demonstrates that for good P removal, nitrate discharged to the anaerobic reactor should be avoided at all costs.

CAN COMPLETE DENITRIFICATION BE ACHIEVED?

When selecting a Phoredox or UCT type process for excess P removal, it is necessary to establish whether or not complete denitrification can be achieved for a selected sludge age (R_s) and maximum specific growth rate of the nitrifiers at 20°C (μ_{nm20}). If it can be achieved for sludge ages less than about 30 days and unaerated sludge mass fractions less than about 0,50 at the minimum process temperature (T_{min}), then a Phoredox process is indicated; if it cannot be achieved, then a UCT type process is indicated.

Provided the wastewater characteristics are favourable, in particular, a low influent TKN/COD ratio, complete denitrification can be achieved *only if the process configuration incorporates a secondary anoxic reactor* e.g. the Bardenpho (Fig 1) and Phoredox (Fig 3) processes: any nitrate not removed by the primary anoxic reactor (f_{x1}) must be removed by the secondary anoxic reactor (f_{x3}) to obtain complete denitrification.

In the Bardenpho process, the maximum anoxic sludge mass fraction available for denitrification, f_{xdm}, is equal to the maximum unaerated sludge mass fraction, f_{xm}. In the Phoredox process, an anaerobic reactor is required for the stimulation of excess P removal, so that f_{xdm} for this process is the difference between f_{xm} and the anaerobic sludge mass fraction f_{xa}, i.e.

$$f_{xdm} = f_{xm}, \text{ for the Bardenpho} \qquad (15a)$$

$$f_{xdm} = f_{xm} - f_{xa}, \text{ for the Phoredox} \qquad (15b)$$

where f_{xm} is given by Eq (2) for a selected R_s, μ_{nmT} and T_{min}.

To check whether or not complete denitrification can be obtained with the maximum *anoxic* sludge mass fraction given by Eq (15 a or b), the following reasoning is followed: In the Bardenpho or Phoredox process, for a fixed underflow s-recycle ratio, the mixed liquor a-recycle ratio governs the distribution of the nitrate from the aerobic reactor between the primary and secondary anoxic reactors - the higher the a-recycle ratio with respect to the s-recycle ratio the greater the proportion of nitrate recycled to the primary anoxic reactor. For the selected a- and s-recycle ratio, the best denitrification performance is obtained when the primary anoxic reactor is just loaded to its denitrification potential. If the primary anoxic reactor is loaded to its denitrification potential, the nitrate concentration in the outflow of the reactor is zero and the nitrate concentration in the aerobic reactor is given by $N_c/(a+s+1)$ i.e. the nitrification capacity diluted into the total flow entering the aerobic reactor. Knowing the nitrate and dissolved oxygen (D.O.) concentrations in the aerobic reactor, the equivalent nitrate load imposed on the primary and secondary anoxic reactors by the selected a- and s-recycles can be calculated. A useful analytical device is to increase the equivalent nitrate load on the secondary anoxic reactor by a factor K_{2T}/K_{3T} so

that the reactor acts like a primary anoxic reactor except that it receives no rapidly biodegradable COD. Now adding the equivalent nitrate load on the primary anoxic to the adjusted equivalent nitrate load on the secondary anoxic reactor, a total equivalent nitrate load is obtained. Because the secondary anoxic reactor has been transformed to act like a primary anoxic reactor, the respective contributions to total denitrification potential by the primary and secondary anoxic reactors need not be known, and maximum anoxic sludge mass fraction (f_{xdm}) can be assumed to be in the form of a primary anoxic reactor. Consequently the process denitrification potential D_{pp} can be calculated by means of Eq (5) with $f_{x1} = f_{xdm}$. Now if the process denitrification potential D_{pp} of the maximum anoxic sludge mass fraction f_{xdm}, is greater or equal to the total equivalent nitrate load, complete denitrification is possible for the selected a- and s-recycle ratios. In contrast, if the D_{pp} of f_{xdm} is less than the total equivalent nitrate load, complete denitrification is not possible for the selected a- and s-recycle ratios, and nitrate will be present in the effluent.

Following the above reasoning and assuming the D.O. concentrations in the a- and s-recycles are d_a and d_s mgO/ℓ respectively, the following equation for the effluent nitrate concentration N_{ne} for the Bardenpho or Phoredox processes can be developed:

$$N_{ne} = \frac{\{\frac{N_c}{a + s + 1} + \frac{d_a}{2,86}\}\{a + \frac{K_{2T}}{K_{3T}}(s + 1)\} + \frac{s.d_s}{2,86} - D_{pp}}{\{\frac{K_{2T}}{K_{3T}} + s(\frac{K_{2T}}{K_{3T}} - 1)\}} \qquad (16)$$

where

D_{pp} = denitrification potential at temperature T°C on the assumption that the maximum anoxic sludge mass fraction f_{xdm} found from Eq (15a or b) is all in the form of a primary anoxic reactor, i.e. D_{pp} is given by Eq (5) with $f_{x1} = f_{xdm}$.

Also, the optimum primary and secondary anoxic sludge mass fractions f_{x1} and f_{x3}, and the total f_{xdt} are given by

$$f_{x1} = \frac{\{\frac{N_c}{a + s + 1} + \frac{d_a}{2,86})a + (N_{ne} + \frac{d_s}{2,86})s - \frac{f_{bs}(1 - P_v Y_h)S_{bi}}{2,86}\}}{\{S_{bi}\ \frac{Y_h R_s}{(1 + b_{hT} R_s)}\ K_{2T}\}} \qquad (17)$$

$$f_{x3} = \frac{\{(s + 1)\left[\frac{N_c}{a + s + 1} + \frac{d_a}{2,86} - N_{ne}\right]\frac{K_{2T}}{K_{3T}}\}}{\{S_{bi}\ \frac{Y_h R_s}{(1 + b_{hT} R_s)}\ K_{2T}\}} \qquad (18)$$

$$f_{xdt} = f_{x1} + f_{x3} \qquad (19)$$

For fixed R_s, μ_{nm20}, T_{min} and wastewater characteristics (from which f_{xm} (Eq 2), f_{xdm} (Eq 15a or b), K_{2T}/K_{3T} (Eqs 7 and 8), N_c (Eq 3) and D_{pp} (Eq 5) are found) and selected D.O. concentrations in the a- and s-recycles, the only unknowns in Eqs (16 to 18) are the a- and s-recycle ratios. The s-recycle ratio is usually specified (at say 1) to obtain satisfactory settling tank performance. Hence N_{ne}, f_{x1} and f_{x3} all depend on the a-recycle ratio only, and hence these three parameters can be calculated for various choices of the a-recycle ratio. If $N_{ne} \leq 0,0$ mgN/ℓ

for some specified s- and selected a-recycle ratios, then complete denitrification is possible at these recycle ratios.

In the solution procedure, if Eq (16) yields $N_{ne} < 0$, N_{ne} must be set equal to zero before substitution into Eqs (17 and 18). When N_{ne} has to be set to zero, it will be noticed that f_{xdt} obtained from Eq (19) is less than the f_{xdm} assumed to calculate D_{pp}. The reason for this is that when $N_{ne} < 0,0$, the denitrification potential of the maximum anoxic sludge mass fraction, f_{xdm}, is greater than the nitrification capacity. By inserting $N_{ne} = 0,0$ in Eqs (17 and 18), these equations give f_{x1} and f_{x3} that will *just* produce complete denitrification for the selected a- and specified s-recycle ratios, so that f_{xdt} is less than f_{xdm}.

For the specified s-recycle ratio, the equations above are valid only for a-recycle ratios falling between a lower and an upper limit: (i) lower limit; the a-recycle ratio must not be lower than that which gives f_{x1} as calculated from Eq (17) less than f_{x1min} as calculated from Eq (9) - if $f_{x1} < f_{x1min}$, the rapidly biodegradable COD is not completely utilized in the primary anoxic reactor; (ii) upper limit; the a-recycle ratio cannot be increased above that which gives f_{x3} from Eq (18) a smaller value than that required to remove only the dissolved oxygen discharged to the secondary anoxic reactor, $D_{p3} \geq (1+s)d_a/2,86$ where D_{p3} is given by Eq (6) - hence the minimum secondary anoxic sludge mass fraction f_{x3min} is given by

$$f_{x3min} = \frac{(1+s)d_a \ (1+b_{hT}R_s)}{(1-f_{us}-f_{up}) \ S_{ti} \ Y_h R_s \ K_{3T} \ 2,86} \qquad (20)$$

Only the a-recycle ratios falling between the lower and upper limits specified above are valid a-recycle ratios.

By analyzing the system with a specified s-recycle ratio for increasing values of valid a-recycle ratios, then if $N_{ne} > 0$, N_{ne} and the subdivision of f_{xdm} into f_{x1} and f_{x3}, or, if $N_{ne} = 0$, the anoxic sludge mass fraction to just obtain $N_{ne} = 0$, f_{xdt}, and its subdivision into f_{x1} and f_{x3}, can be plotted versus the a-recycle ratio.

For design purposes where the process is to operate between temperatures T_{min} and T_{max}, the following sequence of calculations needs to be made to check whether complete denitrification can be achieved and if so, to select the optimal process configuration:

Step 1 : Select wastewater characteristics; S_{ti}, N_{ti}, P_{ti}, f_{bs}, f_{up}, f_{us}, μ_{nm20}, T_{max}, T_{min}.

Step 2 : Select R_s and S_f.

Step 3 : Calculate f_{xm} for T_{min} from Eq (2).

Step 4 : With f_{xm} and R_s calculate S_f for T_{max} from Eq (2).

Step 5 : Estimate N_{te} for T_{max} and T_{min}.

Step 6 : With f_{up} and f_{us}, calculate N_s for T_{max} and T_{min} for selected R_s from Eq (4).

Step 7 : Calculate N_c from Eq (3).

Step 8 : Calculate D_{pp} from Eq (5) for T_{max} and for T_{min} with f_{xdm} given by Eq (15).

Step 9 : Select s, d_a and d_s.

Step 10 : Calculate f_{x1min} from Eq (9) for T_{max} and for T_{min}.

Step 11 : Calculate f_{x3min} from Eq (20) for T_{max} and for T_{min}.

Step 12 : Select the a-recycle ratio and calculate N_{ne} for T_{min} from Eq (16).

Step 13 : If $N_{ne} < 0$, set $N_{ne} = 0$.

Step 14 : With N_{ne} calculate f_{x1}, f_{x3} and f_{xdt} from Eqs (17 to 19).

Step 15 : Check that $f_{x1} \geq f_{x1min}$ and $f_{x3} \geq f_{x3min}$. If not, discard selected a-recycle ratio as invalid.

Step 16 : Repeat steps 12 to 15 for different a-recycle ratios,

Step 17 : Repeat steps 12 to 16 for T_{max}.

Following the procedure above, the design curves for a Bardenpho and a Phoredox process were calculated for a sludge age of 25 days treating the raw and settled wastewater (characteristics listed in Table 2) for a temperature range of 14°C to 20°C. Design curves for the Bardenpho process only are shown for both the raw and settled wastewater at 14°C in Fig 13 and 20°C in Fig 14. Key response characteristics for both the Bardenpho and the Phoredox processes are listed in Table 3.

The analysis as to whether or not complete denitrification can be achieved must be undertaken at the *lowest expected temperature (T_{min})*, because the denitrification potential D_{pp} decreases with decrease in temperature. If complete denitrification can be obtained at T_{min} (i.e. $N_{ne} \leq 0$ from Eq 16 for some valid a-recycle ratio at the specified s-recycle ratio), then f_{x1} is fixed at the *highest expected* temperature (T_{max}). In repeating the calculation at T_{max} it will be found that f_{xdt} at T_{max} is less than f_{xdt} at T_{min}, and for a certain a-recycle ratio, there will be a minimum f_{xdt}* (compare Figs 13a and 14a). The f_{x1} value corresponding to the minimum f_{xdt} at T_{max} fixes the primary anoxic sludge mass fraction for both T_{max} and T_{min}. For the raw wastewater complete denitrification can be achieved in the Bardenpho process (Fig 13a) for any a-recycle ratio > 1,8. At 20°C (Fig 14a) a minimum f_{xdt} of 0,37 for complete denitrification occurs at a mixed liquor a-recycle ratio of 4,2 and the corresponding f_{x1} and f_{x3} are 0,16 and 0,21 respectively. Hence f_{x1} is fixed at 0,16. Now if f_{x3} is fixed at the value corresponding to f_{x1} at T_{max} i.e. 0,21, then f_{xdt} will be insufficient to achieve complete denitrification at T_{min}, because for a fixed f_{x1}, f_{xdt} at T_{max} is less than f_{xdt} at T_{min}. Hence f_{x3} is fixed at T_{min} at the value corresponding to the fixed $f_{x1} = 0,16$ i.e. $f_{x3} = 0,24$ (Fig 13a). Hence $f_{xdt} = 0,40$ for complete denitrification at 14°C and 20°C. With f_{x1} and f_{x3} fixed for both T_{max} and T_{min}, the optimum performance of the process is achieved when it is operated at the a-recycle ratio corresponding to the fixed f_{x1} value, this a-recycle ratio being the optimum a_o, i.e. at 14°C $a_o = 3,3$ (Fig 13a) and for 20°C, $a_o = 4,2$ (Fig 14a). It should be noted that with f_{x1} and f_{x3} fixed, (i) a_o decreases with decrease in temperature because D_{p1} decreases with decrease in temperature (compare Figs 13a and 14a) and (ii) the use of *any a-recycle ratio other than a_o results in poorer denitrification performance:* if $a < a_o$, D_{p1} is not fully exploited and if $a > a_o$ unnecessarily large quantities of D.O. are discharged to the primary anoxic reactor.

In the design of a Bardenpho or Phoredox process for a selected sludge age, if it is found that the total anoxic sludge mass fraction for complete denitrification f_{xdt} is less than the maximum allowed f_{xdm}, the following options are open:

1) f_{x1} and f_{x3} can be increased to give a total anoxic sludge mass fraction equal to f_{xdm} which introduces a factor of safety for denitrification, the magnitude of which is equal to f_{xdm}/f_{xdt}.

2) The sludge age can be reduced so that f_{xdm} becomes equal to f_{xdt}. The lower sludge age will allow a saving in process volume (see Fig 16). This lower sludge age R_s, can be estimated as follows: set f_{xdm} equal to f_{xdt} required for complete denitrification at T_{min}; determine f_{xm} from Eq (15); with f_{xm}

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*If T_{max} is less than about 18°C, a clear minimum cannot be discerned (see Fig 13a for 14°C). In this event any reasonable f_{x1} can be selected with the proviso that complete utilization of the rapidly biodegradable COD can be *assured* even with a significant decrease in $K_{1}20$ (see Eqs 9 and 10). The existence of a minimum, and the temperatures above which it becomes discernable, depends much on the choice of the D.O. concentration in the recycles d_a and d_s.

TABLE 3 Summary of design calculations for the Bardenpho and Phoredox processes treating raw or settled wastewater at 25 days sludge age. Wastewater characteristics given in Table 2.

Parameter	Symbol	Units	Raw Wastewater				Settled Wastewater			
			Bardenpho		Phoredox		Bardenpho		Phoredox	
Temperature	T	°C	14	20	14	20	14	20	14	20
Safety factor	S_f		1,3	2,3	1,3	2,3	1,3	2,3	1,3	2,3
Max.unaerated sludge mass	f_{xm}		0,50	0,50	0,50	0,50	0,50	0,50	0,50	0,50
Effluent TKN	N_{te}	mgN/ℓ	3,0	2,0	3,0	2,0	3,0	2,0	3,0	2,0
N for sludge production	N_s	mgN/ℓ	12,6	12,2	12,6	12,2	5,7	5,4	5,7	5,4
Nitrification capacity	N_c	mgN/ℓ	32,4	33,8	32,4	33,8	32,3	33,6	32,3	33,6
Anaerobic sludge mass	f_{xa}		0	0	0,10	0,10	0	0	0,10	0,10
Max. anoxic sludge mass	f_{dxm}		0,50	0,50	0,40	0,40	0,50	0,50	0,40	0,40
Max. denit. potential	Dpp	mgN/ℓ	42,8	53,6	37,0	45,7	30,9	37,7	27,2	32,8
D.O. in a-recycle	d_a	mgO/ℓ	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0
D.O. in s-recycle	d_s	mgO/ℓ	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0
Underflow recycle ratio	s		1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0
Prim. anoxic sludge mass	f_{x1}		0,16	0,16	0,16	0,16	0,34	0,34	0,28	0,28
Sec. anoxic sludge mass	f_{x3}		0,24	0,21	0,24	0,21	0,16	0,16	0,12	0,12
Total anoxic sludge mass	f_{xdt}		0,40	0,37	0,40	0,37	0,50	0,50	0,40	0,40
Optimum a-recycle ratio	a_o		3,3	4,2	3,3	4,2	2,4	4,2	1,4	2,5
Effluent nitrate	N_{ne}	mgN/ℓ	0,0	0,0	0,0	0,0	5,1	2,9	8,0	6,0
Nitrate recycled to anaerobic reactor	N_{ns}	mgN/ℓ	-	-	0,0	0,0	-	-	8,0	6,0
Readily bio. COD in anaerobic reactor	S_{bsa}	mgCOD/ℓ	-	-	57,5	57,5	-	-	16,5	25,1
Propensity factor	P_f	mgCOD/ℓ	0,0	0,0	3,25	3,25	0,0	0,0	0,0	0,086
γ coefficient	γ	mgP/ mgVASS	0,06	0,06	0,22	0,22	0,06	0,06	0,06	0,066
P removal	P_s	mgP/ℓ	3,5	3,3	9,3	8,3	1,9	1,7	1,9	1,8
Effluent P concentration	P_{te}	mgP/ℓ	6,5	6,7	0,7	1,7	6,6	6,8	6,6	6,7

calculate R_s from Eq (2); to check repeat step by step procedure for the new R_s.

3) For the Phoredox process, f_{xa} can be increased to improve excess P removal, so that $f_{xdm} = f_{xdt}$ from Eq (15b).

Options (2) and (3) above are not recommended as these exclude a factor of safety in denitrification. Exclusion of a factor of safety is not critical for N removal in the Bardenpho process because it achieves efficient N removal with respect to the other N removal process (i.e. the MLE process) up to an effluent nitrate concentration of about 6 mgN/ℓ. However, exclusion of a factor of safety on denitrification for the Phoredox process may have serious consequences because the discharge of *any*

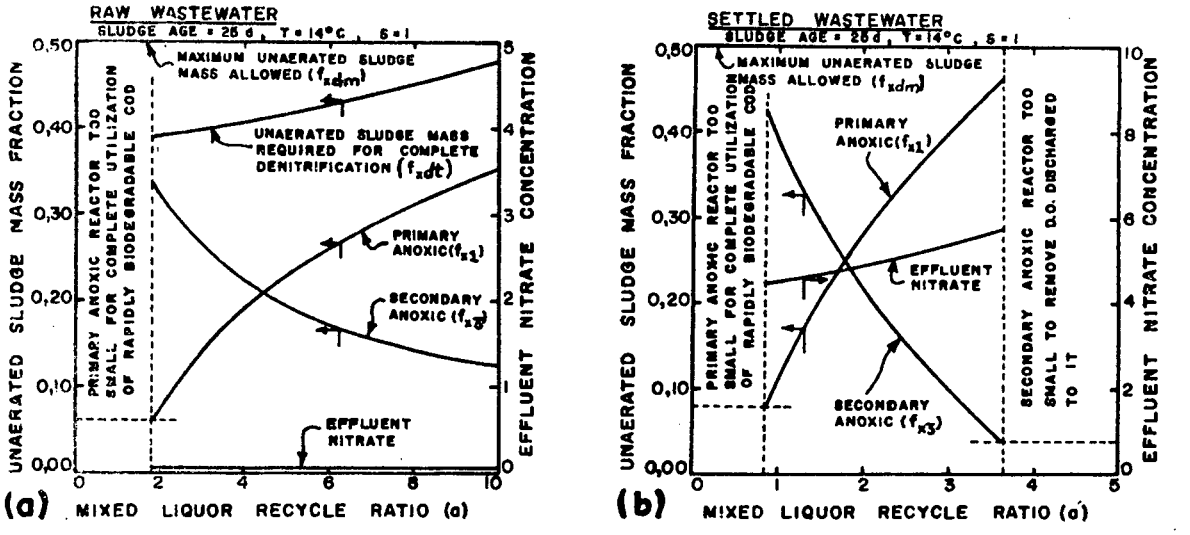

Fig 13 Primary (f_{x1}), secondary (f_{x3}), total(f_{xdt}) and maximum permissible (f_{xdm}) unaerated sludge mass fractions and effluent nitrate concentration versus mixed liquor recycle ratio for the Bardenpho process at 25 days sludge age and 14°C for raw (Fig 13a) and settled (Fig 13b) wastewaters

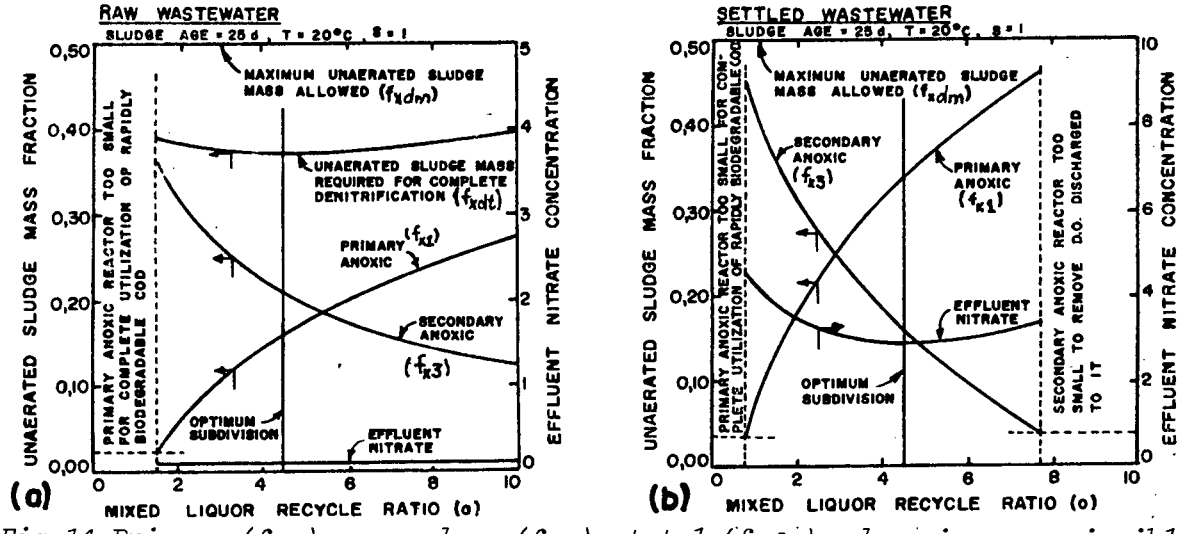

Fig 14 Primary (f_{x1}), secondary (f_{x3}), total (f_{xdt}) and maximum permissible (f_{xdm}) unaerated sludge mass fractions and effluent nitrate concentration versus mixed liquor recycle ratio for the Bardenpho process at 25 days sludge age and 20°C for raw (Fig 14a) and settled (Fig 14b) wastewaters

nitrate to the anaerobic reactor severely reduces the P removal obtainable in the process (Fig 12). For example, in the calculations above, for the raw wastewater, it was found that a total anoxic sludge mass fraction f_{xdt} of only 0,40 is required to obtain complete denitrification at the minimum temperature whereas a total unaerated sludge mass fraction f_{xm} of 0,50 is allowed. Now if N removal only is considered important, a Bardenpho process is appropriate and (i) if a factor of safety is required for complete denitrification, option 1 above can be taken i.e. f_{x1} and f_{x3} are increased such that $f_{x1} + f_{x3} = f_{xm} = 0,50$, or, (ii) if no factor of safety for complete denitrification is required, option 2 above can be taken i.e. the sludge age can be reduced such that $f_{xm} = f_{xdt} = 0,40$. However if both N and P removal are required, then the largest anaerobic sludge mass fraction f_{xa} that can be allowed in a Phoredox process is 0,10 because 0,40 is required to achieve complete denitrification. With $f_{xa} = 0,10$ and $N_{ns} = 0,0$ mgN/ℓ, then for the raw wastewater at 14°C and $R_s = 25$ days, we have from Eqs (11-14) $S_{bsa} = 57,5$ mgCOD/ℓ, $P_f = 3,25$ mgCOD/ℓ and $\gamma = 0,22$ mgP/mgVASS giving a P removal $P_s = 9,3$ mgP/ℓ so that

with an influent P_{ti} of 10 mgP/ℓ, an effluent P_{te} of only 0,7 mgP/ℓ is obtained (see Table 3). However, setting f_{xa} at its maximum value of 0,10 will leave the Phoredox process in a critical condition because to achieve the high P removal of 9,3 mgP/ℓ, complete denitrification *must* be assured at all times, but this cannot be guaranteed as there is no factor of safety on the denitrification. To introduce a factor of safety on the denitrification, f_{x1} can be increased at the expense of f_{xa}, but this will be at a cost of a reduced P removal (see Eq 12). Alternatively the sludge age can be increased thereby allowing a larger f_{xm} (Eq 2); however, the increase in sludge age will be at the expense not only of an increased process volume (Fig 16) but also a reduced P removal (Fig 11). Clearly the raw wastewater influent TKN/COD ratio i.e. 0,08 mgN/mgCOD,is just on the limit for the successful implementation of the Phoredox process - any small increase in TKN/COD ratio will result in incomplete denitrification,discharge of nitrate to the anaerobic reactor and severe deterioration in P removal (Fig 12).

In a Bardenpho or Phoredox process, if it is found that complete denitrification cannot be obtained (i.e. $N_{ne} > 0,0$ from Eq 16 for all valid a-recycle ratios at the specified s-recycle ratio), nitrate will be present in the effluent and it will be found that f_{xdt} obtained from Eq (19) is equal to f_{xdm}. Generally, if the objective is N removal by means of a Bardenpho process, then this process will be appropriate only if N_{ne} is less than about 5 to 7 mgN/ℓ; when $N_{ne} > 5$ to 7 mgN/ℓ, the MLE process (Fig 2) for N removal will be the more appropriate process for the particular wastewater. If the objective is N *and* P removal by using a Phoredox process, this process will not be appropriate when $N_{ne} > 0$ because excess P removal will be reduced by the discharge of nitrate to the anaerobic reactor via the underflow s-recycle - the only viable processes for obtaining excess P removal when $N_{ne} > 0$ will be the UCT processes.

The criteria for selection of a process set out above can now be applied to the examples listed in Table 3: (1) For the Bardenpho process *treating the settled wastewater*, complete denitrification cannot be achieved at either 14°C or 20°C for any valid a-recycle ratio, with $f_{xdt} = f_{xm} = 0,50$ (Figs 13b and 14b, see also Table 3). At 14°C (Fig 13b), N_{ne} is approximately 5 mgN/ℓ depending on the a-recycle ratio, and at 20°C, a minimum $N_{ne} = 2,9$ mgN/ℓ at an a-recycle ratio of 4,2 is obtained. Because $N_{ne} < 5$ to 7 mgN/ℓ at T_{min}, a Bardenpho process will be appropriate for N removal and the optimum subdivision of the unaerated sludge mass fraction is found as follows: f_{x1} and f_{x3} are fixed at T_{max} at the values corresponding to the minimum N_{ne}*, i.e. for 20°C (Fig 14b), $f_{x1} = 0,34$ and $f_{x3} = 0,16$. With f_{x1} and f_{x3} fixed, the optimum a-recycle ratio a_o at 20°C (Fig 14b) is 4,2 giving $N_{ne} = 2,9$ mgN/ℓ; a_o at 14°C (Fig 13b) is 2,4 giving $N_{ne} = 5,1$ mgN/ℓ. (2) For the Phoredox process *treating the settled wastewater* at $R_s = 25$ days, with $f_{xa} = 0,10$ and $f_{xdm} = 0,40$ (see Table 3), a minimum N_{ne} of 6 mgN/ℓ is obtained at 20°C with $f_{x1} = 0,28$, $f_{x3} = 0,12$ and $a_o = 2,5$ and $N_{ne} = 8,0$ mgN/ℓ at 14°C with $a_o = 1,4$. With 8,0 mgN/ℓ nitrate in the effluent and underflow s-recycle, and assuming the s-recycle ratio is specified at 1 and contains a D.O. concentration of 1 mgO/ℓ, then from Eq (13), the rapidly biodegradable COD concentration in the anaerobic reactor (S_{bsa}) is 16,5 mgCOD/ℓ, which is far below the minimum to achieve excess P removal. Hence, from Eq (12), the propensity factor P_f is 0 and, from Eq (14) the γ coefficient is at its minimum of 0,06 mgP/mgVASS. With $\gamma = 0,06$, the P removal (P_s) at $R_s = 25$ at 14°C from Eq (11) is 1,9 mgP/ℓ. Because the influent P (P_{ti}) for the settled wastewater is 8,5 mgP/ℓ (Table 2), the effluent P (P_{te}) is 8,5 - 1,9 = 6,6 mgP/ℓ. Similarly poor P removal is also obtained at 20°C (see Table 3).Clearly

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*If T_{max} is less than 18°C, a clear minimum cannot be discerned (see Fig 13b at 14°C). In this event, any reasonable f_{x1} can be selected with the proviso that complete utilization of the rapidly biodegradable COD can be assured even with a significant decrease in K_{120} (see Eqs 9 and 10). The existence of a minimum, and the temperature above which it becomes discernable, depends much on the choice of the D.O. concentrations in the recycles, d_a and d_s.

the Phoredox process will not function as an efficient P removal facility due to incomplete denitrification.

Usually complete denitrification cannot be obtained once the influent TKN/COD is above 0,07 to 0,08 mgN/mgCOD. For TKN/COD ratios above 0,08 mgN/mgCOD, the UCT processes are the only viable processes for achieving excess P removal.

WHEN COMPLETE DENITRIFICATION CANNOT BE ACHIEVED

When the wastewater characteristics are such that complete denitrification cannot be obtained, the only viable processes for excess P removal are the UCT type processes. In the design of these processes, the complicating factor, that of determining the effluent nitrate concentration in order to estimate the P removal, is absent because the UCT processes allow positive exclusion of nitrate from the anaerobic reactor despite the presence of an effluent nitrate concentration. This facilitates the design of the processes in that N and P removal can be dealt with separately.

With regard to design of N removal in the UCT processes, the N removal behaviour of these processes is similar to that of the MLE process except that for the same maximum unaerated sludge mass fraction (f_{xm}), the maximum anoxic sludge mass fraction for denitrification (f_{xdm}) for the UCT processes is less than that for the MLE process due to the requirement of an anaerobic reactor for excess P removal, i.e. Eq (15a) applies to the MLE process and Eq (15b) to the UCT type processes. For the selected R_S, Sf, μ_{nm20}, T_{min} and wastewater characteristics, f_{xm} (Eq 2), N_C (Eq 3), f_{xdm} (Eq 15a or b) and D_{pp} (Eq 5 with $f_{xl} = f_{xdm}$) for the MLE or UCT processes are found by the identical procedure as for the Bardenpho or Phoredox processes (i.e. steps 1 to 8). For the MLE and UCT type processes, the best denitrification performance is obtained when the anoxic reactor is just loaded with nitrate to its denitrification potential. For a specified s-recycle ratio, the mixed liquor a-recycle ratio which loads the anoxic reactor to its denitrification potential is the optimum a-recycle ratio, a_o, and will yield the minimum effluent nitrate concentration. When the nitrate load imposed on the anoxic reactor by the a- and s-recycles (including D.O. concentrations in the a- and s-recycles of d_a and d_s mgO/ℓ respectively), is less than or equal to the denitrification potential (D_{pp}), the nitrate concentration in the outflow of the anoxic reactor is zero and that in the aerobic reactor and effluent is $N_C/(a+s+1)$ i.e. the nitrification capacity "diluted" into the total flow entering the aerobic reactor. Equating the nitrate load on the anoxic reactor imposed by the a- and s-recycles (including the D.O. in the recycles) to the denitrification potential D_{pp} and solving for the a-recycle ratio yields a_o;

$$a_o = \{-B + \sqrt{B^2 + 4AC}\}/(2A) \qquad (21)$$

where $A = d_a/2,86$

$B = N_C - D_{pp} + \{(s+1)d_a + s.d_s\}/2,86$

$C = (s+1)(D_{pp} - sd_s/2,86) - sN_C$

The effluent nitrate concentration N_{ne} for any a-recycle ratio less than or equal to a_o is given by Eq (22) but will be a minimum when $a = a_o$, i.e.

$$N_{ne} = N_C/(a + s + 1) \text{ mgN}/\ell \qquad (22)$$

In the design of an MLE process, it will be found the lower N_C is with respect to D_{pp} (i.e. the lower the influent TKN/COD ratio) the lower the N_{ne} and the higher the a_o. In practice, to operate an MLE process with an a_o-recycle ratio greater than 6:1 will be uneconomical: the increase in nitrate removal by increasing a_o from 6 to 10 is only 5% and, therefore, will not be cost-effective with respect to the increased pumping costs. Hence, the N removal of the MLE process is restricted by a maximum a-recycle ratio of say 6, which results in a minimum N_{ne} of 5 to

7 mgN/ℓ. This restriction on the MLE process will not be a problem in practice because high a_o are only required for wastewaters with low TKN/COD ratios (< 0,10 mgN/mgCOD) and these wastewaters are more effectively treated in a Bardenpho process (see section above). Alternatively, if near-complete or complete N removal is not essential, the sludge age can be reduced; for a fixed TKN/COD ratio this reduces D_{pp} (because f_{xm} is reduced) with respect to N_c and hence reduces a_o. The optimum R_s for the fixed TKN/COD ratio can be found using the procedure of van Haandel *et al.* (1982).

In the design for N and excess P removal in the UCT type processes, the conditions in the anaerobic reactor for excess P removal are independent of the denitrification behaviour of the processes for TKN/COD ratios up to about 0,14 mgN/mgCOD. The rapidly biodegradable COD concentration in the anaerobic reactor (S_{bsa}) can be found directly from Eq (13a and c) without the need for selecting R_s or μ_{mn20}: S_{bsa} depends only on the influent COD strength (S_{ti}), the rapidly biodegradable COD fraction (f_{bs}) and the r-recycle ratio from the anoxic to the anaerobic reactor. The r-recycle ratio usually is selected at 1:1; higher ratios lead to greater dilution of S_{bsa} with a concomitant reduction in P removal and lower values lead to inordinately large anaerobic reactor *volume* fractions with respect to the anaerobic sludge *mass* fractions (see Eqs 27 to 30). Selecting r = 1 and the nitrate and D.O. concentrations in the r-recycle of say 1 mgN/ℓ and 1 mgO/ℓ to include a factor of safety for excess P removal, then S_{bsa} can be calculated from Eqs (13a and c), and will remain unchanged irrespective of the temperature. Knowing S_{bsa}, the propensity factor P_f can be calculated from Eq (12) for a selected anaerobic sludge mass fraction f_{xa}, and from the P_f value, the γ coefficient can be calculated from Eq (14). Knowing γ, the P removal from the particular wastewater can be calculated from Eq (11) for a selected sludge age (R_s). The P removal should be determined at T_{max} because, for a constant S_{bsa} or γ, the P removal at T_{max} is less than at T_{min} (Fig 11). Hence, for various values of f_{xa}, the P removal at different sludge ages can be calculated, and estimates of f_{xa} and R_s giving the desired or optimal P removal can be found. In selecting f_{xa}, it is recommended that f_{xa} should not be less than 0,10 and not greater than 0,20: for $f_{xa} < 0{,}10$, the P removal usually will be inadequate even at relatively short sludge ages for normal wastewaters, particularly for settled wastewaters; for $f_{xa} > 0{,}20$ no experimental response data are available so that, it may be risky to accept $f_{xa} > 0{,}20$. At $f_{xa} = 0{,}20$, the process has been found to operate satisfactorily (Siebritz *et al.* 1982). With regard to selecting R_s, cognizance must be taken of its effect on the maximum unaerated sludge mass fraction f_{xm} (Eq 2) because, with f_{xa} fixed, f_{xm} fixes the maximum anoxic sludge mass fraction f_{xdm} (Eq 15b) which, in turn, governs the degree of denitrification that can be achieved.

Once f_{xa} and R_s are selected, the denitrification can be calculated by applying the design equations for N removal in the MLE process, except that f_{xdm} is given by the difference between f_{xm} and f_{xa} (see Eq 15b).

For design purposes, where the process is to operate between temperatures T_{min} and T_{max}, the following sequence of calculations is recommended to facilitate selection of the optimal process configuration for N and P removal in the UCT process:

Step 1 : Select wastewater characteristics; S_{ti}, N_{ti}, P_{ti}, f_{bs}, f_{up}, f_{us}, μ_{nm20}, T_{max}, T_{min}.

Step 2 : Select r (usually 1,0) and N_{nr} and d_r (say 1 mg/ℓ each).

Step 3 : Calculate S_{bsa} from Eqs (13a and c).

Step 4 : Select f_{xa} (between 0,10 and 0,20).

Step 5 : Calculate P_f from Eq (12) and γ from Eq (14).

Step 6 : Select R_s.

Step 7 : Calculate P_s from Eq (11) for T_{max} and for T_{min}.

Step 8 : Select S_f.

Step 9 : Calculate f_{xm} for T_{min} from Eq (2).

Step 10 : With f_{xm} and R_S calculate S_f for T_{max} from Eq (2).

Step 11 : Estimate N_{te} for T_{max} and T_{min}.

Step 12 : With f_{up} and f_{us}, calculate N_s for T_{max} and T_{min} for selected R_S from Eq (4).

Step 13 : Calculate N_c from Eq (3).

Step 14 : Calculate D_{pp} from Eq (5) for T_{max} and for T_{min} with f_{xdm} given by Eq (15b).

Step 15 : Select s, d_a and d_s.

Step 16 : Calculate a_o from Eq (21) and N_{ne} from Eq (22).

Step 17 : Are P_S and N_{ne} adequate? If P_S is too low, increase f_{xa} or reduce R_S - these changes will increase N_{ne}; If P_S is too high, decrease f_{xa} or increase R_S - these changes will decrease N_{ne}.

Step 18 : Repeat from steps 4 to 16 until required or optimal P_S and N_{ne} is obtained.

The design calculations for the UCT process are illustrated by following the step by step procedure for the raw and settled wastewater characteristics listed in Table 2 at 14°C and 20°C for a sludge age of 20 days and an anaerobic sludge mass fraction of 0,15. The results are listed in Table 4.

For the *raw wastewater* at 14°C and 20°C, more P can be removed than is present in the influent so that complete P removal is attained with a factor of safety. The effluent nitrate concentrations are 6,5 mgN/ℓ at 14°C and 4,4 mgN/ℓ at 20°C. Comparing these results with those of the Phoredox process (Table 3), it can be seen that the Phoredox does not quite attain complete P removal but attains complete N removal, so that it would appear that the effluent quality from the Phoredox process is better than that from the UCT process. However the Phoredox requires a sludge age of 25 days whereas the UCT process requires only 20 days leading to a 15% saving in process volume (Fig 16). Furthermore the UCT process incorporates a factor of safety for complete P removal (i.e. d_r = 1,0 mgO/ℓ, N_{nr} = 1,0 mgN/ℓ and $P_S > P_{ti}$) whereas the P removal in the Phoredox process is dependent on the attainment of complete N removal without a factor of safety so that *any* increase in TKN/COD ratio will severely reduce the P removal. Consequently, although the UCT process yields a poorer N removal, the P removal will be attained with greater surety. Furthermore, if the actual TKN/COD ratio is greater than that accepted for design, the P removal can be nevertheless attained by operational adjustments in the process, up to TKN/COD ratios up to about 0,13 mgN/mgCOD. The upper limiting TKN/COD ratio can be calculated by testing higher TKN/COD ratios on the final configuration.

For the *settled wastewater*, the P removal (P_S) at 14°C is 6,7 mgP/ℓ and at 20°C is 5,9 mgP/ℓ, leaving 1,8 and 2,6 mgP/ℓ in the effluent at 14°C and 20°C respectively and the effluent nitrate concentrations (N_{ne}) are 11,6 and 9,9 mgN/ℓ at 14°C and 20°C respectively. If P_S is insufficient, then f_{xa} can be increased to its maximum of 0,20, but the increase will result in a poorer N removal, i.e. at f_{xa} = 0,20, P_S = 7,6 mgP/ℓ and N_{ne} = 13,1 mgN/ℓ at 14°C and P_S = 6,6 mgP/ℓ and N_{ne} = 12,0 mgN/ℓ at 20°C. If the N removal at f_{xa} = 0,20 is insufficient, then R_S can be increased to improve the N removal, but the increase in R_S will cause a decrease in P removal and also will be at the expense of a larger process volume (see Fig 16), i.e. at R_S = 25 days, P_S = 6,4 mgP/ℓ and N_{ne} = 10,1 mgN/ℓ at 14°C and P_S = 5,6 mgP/ℓ and N_{ne} = 7,9 mgN/ℓ at 20°C. Comparing the P and N removals at R_S = 20 days and f_{xa} = 0,15 with those at R_S = 25 days and f_{xa} = 0,20, it can be seen that P_S in the former design is slightly higher than in the latter and that the N removal in the former is slightly poorer than in the latter. This shows that for high P removals

TABLE 4 Summary of design calculations for the UCT processes treating raw and settled wastewaters at 20 days sludge age. Wastewater characteristics given in Table 2.

Parameter	Symbol	Units	Raw Wastewater		Settled Wastewater	
Temperature	T	°C	14	20	14	20
Nitrate in r-recycle	N_{nr}	mgN/ℓ	1,0	1,0	1,0	1,0
D.O. in r-recycle	d_r	mgO/ℓ	1,0	1,0	1,0	1,0
Influent biod. COD	S_{bi}	mgCOD/ℓ	492	492	317	317
Rapidly biod. COD fraction	f_{bs}	-	0,24	0,24	0,33	0,33
r-recycle ratio	r	-	1,0	1,0	1,0	1,0
Rapidly biod. COD in anaer.	S_{bsa}	mgCOD/ℓ	53,3	53,3	46,5	46,5
Propensity factor	P_f	mgCOD/ℓ	4,24	4,24	3,22	3,22
γ coefficient	γ	mgP/ mgVASS	0,25	0,25	0,22	0,22
P removal	P_s	mgP/ℓ	12,1	10,7	6,7	5,9
Effluent P	P_{te}	mgP/ℓ	0,0	0,0	1,8	2,6
Factor of safety	S_f	-	1,3	2,4	1,3	2,4
Max. unaerated sludge mass	f_{xm}	-	0,40	0,40	0,40	0,40
Effluent TKN	N_{te}	mgN/ℓ	3,0	2,0	3,0	2,0
N for sludge production	N_s	mgN/ℓ	13,2	12,8	6,1	5,8
Nitrification capacity	N_c	mgN/ℓ	31,8	33,2	31,9	33,2
Max. anoxic sludge mass	f_{xdm}	-	0,25	0,25	0,25	0,25
Denitrification potential	D_{pp}	mgN/ℓ	27,7	33,0	21,2	24,6
Underflow recycle ratio	s	-	1,0	1,0	1,0	1,0
D.O. in a-recycle	d_a	mgO/ℓ	2,0	2,0	2,0	2,0
D.O. in s-recycle	d_s	mgO/ℓ	1,0	1,0	1,0	1,0
Opt. a-recycle ratio	a_o	-	2,91	5,5	0,75	1,35
Effluent nitrate	N_{ne}	mgN/ℓ	6,5	4,4	11,6	9,9

it is preferable to have short sludge ages rather than large f_{xa} values and that to obtain the improved P removal, some N removal must be sacrificed. Clearly in the UCT process, good P or N removal can be traded off against each other depending on the critical nutrient to be removed, by appropriate adjustment of f_{xa} and R_s; once f_{xa} and R_s are fixed the removals of N and P per unit influent COD are fixed so that the effluent N and P then depends only on the content of N and P in the influent with respect to the COD strength i.e. the TKN/COD and P/COD ratios.

Comparing the N and P removals attainable treating raw wastewater with that attainable treating settled wastewater, it can be seen that because primary sedimentation increases the P/COD and TKN/COD ratios, the high removals of P and N that can be attained treating raw wastewater cannot be attained treating settled wastewater. However, the high P and N removals attainable treating raw wastewater compared to

those treating settled wastewater is at the expense of significantly larger process volumes (≅ 100% larger, see Fig 16) and increased total oxygen demand (≅ 30% more, see Fig 17).

Having completed the design for the UCT process, if the influent TKN/COD ratio is less than about 0,11 to 0,12 mgN/mgCOD, the process may be converted to a modified UCT process (Fig 6). The conversion is done by subdividing the *anoxic* sludge mass fraction (f_{xdm}) into two sub-fractions; the first is usually allocated a sludge mass fraction f_{xd1} of about 0,10, and the second, f_{xd2}, having the remaining sludge mass fraction i.e. $f_{xd2} = f_{xdm} - f_{xd1}$. Having made this subdivision, the possibility of operating the modified UCT process (Fig 6) as a UCT process (Fig 5) is not excluded; by making provision that the r-recycle flow to the anaerobic reactor can be taken from either the first or the second anoxic reactors, the process can be operated as either a modified UCT or a UCT process (Fig 15). The advantages of operating the process as a modified UCT process were set out in detail earlier.

It is necessary to check whether or not the modified UCT/UCT process combination can be operated as a modified UCT process. For successful operation of the modified process, the denitrification potential of the first anoxic reactor must be greater than, or at least equal to the equivalent nitrate load on the reactor at the *minimum expected temperature* (T_{min}). The denitrification potential is calculated by substituting $f_{xd1} = 0,10$ for f_{x1} in Eq (5). The equivalent nitrate load is found from the effluent nitrate concentration (N_{ne}) from the UCT process, the s-recycle ratio and the D.O. concentration in the s-recycle (d_s) i.e. the equivalent nitrate load is $s(N_{ne} + d_s/2,86)$. For TKN/COD ratios < 0,12 mgN/mgCOD, it will be found that the denitrification potential is sufficient to denitrify the equivalent nitrate load with a reasonable factor of safety (S_{fd}) e.g. at 14°C and R_s = 20 days (see Table 4), for the raw wastewater D_p = 19,4 mgN/ℓ for f_{xd1} = 0,10 and the equivalent nitrate load is 6,8 mgN/ℓ for N_{ne} = 6,5 mgN/ℓ, s = 1 and d_s = 1,0 mgO/ℓ and hence the factor of safety S_{fd} = 19,4/6,8 = 2,8; for the settled wastewater, D_p = 15,8 mgN/ℓ and the equivalent nitrate load is 11,9 mgN/ℓ for N_{ne} = 11,6 mgN/ℓ, s = 1 and d_s = 1,0 mgO/ℓ and hence S_{fd} = 1,33.

By setting $f_{xd1} = 0,10$, usually it will be found that the reactor is sufficiently large for complete utilization of the influent rapidly biodegradable COD (S_{bsi}). This can be checked by means of Eq (9). If T_{min} is less than 14°C, it may be found from Eq (9) that 0,10 is insufficient for complete utilization of the S_{bsi}. In this event, f_{xd1} can be increased slightly to a maximum of 0,12. Values of $f_{xd1} > 0,12$ are not recommended because for temperatures > T_{min}, the reactor will be over-designed leading to a reduced nitrogen removal efficiency of the process. By designing the first anoxic reactor (f_{xd1}) to allow the possibility of complete or near complete utilization of the S_{bsi}, the process can achieve excess P removal up to the TKN/COD ratio at which S_{bsi} is completely utilized. This TKN/COD ratio can be calculated by trial and error by testing increasing TKN/COD ratios on the process.

Generally it will be found that the higher the TKN/COD ratio, the lower the factor of safety S_{fd} for complete denitrification of the equivalent nitrate load on the first anoxic reactor. When S_{fd} < 1,1, the prospect of operating the modified UCT/UCT process combination as a modified UCT process has little merit. This limit is strongly dependent on the influent rapidly biodegradable COD fraction f_{bs}: For normal f_{bs} ratios in raw wastewaters of 0,20 to 0,25, it will be found that S_{fd} is less than 1,1 for TKN/COD ratios above 0,11 to 0,12 mgN/mgCOD at a minimum temperature of 14°C. When the f_{bs} fraction and TKN/COD ratio of the influent are such that operation of the modified UCT process is not possible then it must be operated as a UCT

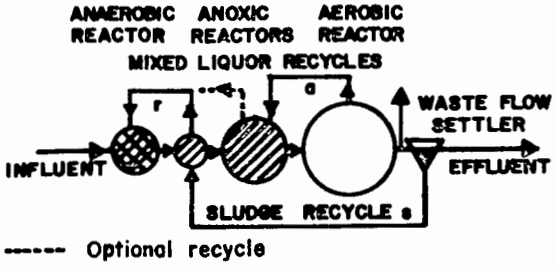

Fig 15 The modified UCT/UCT process combination for biological P and N removal

process. In the UCT process, if the a-recycle ratio is too low to produce an actual anoxic retention time lower than 1 hour, poor sludge settling characteristics are likely to be obtained, and have to be taken into account in the design of the secondary settling tanks.

When the influent rapidly biodegradable COD fraction and TKN/COD ratio are such that operation of a modified UCT process is possible, the mixed liquor a-recycle ratio is set at the greater value of two lower limits i.e. (1) that which loads the secondary anoxic reactor to its denitrification potential or (2) that which will produce an actual anoxic retention time of less than 1 hour. The first limit is calculated with the aid of Eq (21) except that D_{pp} is replaced by the denitrification potential of the *second* anoxic reactor, which can be calculated by substituting the anoxic sludge mass fraction of the second anoxic reactor f_{xd2} for f_{x1} in Eq (5). The second limit is found by calculating the volume of the second anoxic reactor as set out below (see Eqs 26 to 30) and with the specified s-recycle ratio and influent flow rate, finding the a-recycle ratio which would produce an actual retention time of 1 hour.

PROCESS VOLUME REQUIREMENTS AND OXYGEN DEMAND

(1) Process Volume Requirements

Having determined the subdivision of the sludge mass into anaerobic, anoxic and aerobic fractions for optimal removals of N and P for the particular wastewater characteristics, the actual sludge mass in the process needs to be calculated to determine the volumes of the reactors. The mass of volatile sludge (MLVSS) in an activated sludge process (MX_v) is given by Marais and Ekama (1976) as

$$MX_v = Q.S_{ti} \left\{ \frac{(1-f_{us}-f_{up})\ Y_h\ R_s}{(1 + b_{hT}R_s)} (1+fb_{hT}R_s) + \frac{f_{up}}{P_v} \right\} \quad (kgVSS) \qquad (23)$$

From Eq (23), MX_v can be seen to be a function of the sludge age and directly proportional to the daily COD mass load ($Q.S_{ti}$). The volume (V_p) of the process follows from a particular choice of the mean process MLVSS concentration ($\bar{X}_v$) i.e.

$$V_p = MX_v/\bar{X}_v \qquad (24)$$

and the average nominal hydraulic retention time (R_{hn}) is found from the average flow per day (Q) i.e.

$$R_{hn} = V_p/Q. \quad (d) \qquad (25)$$

From Eqs (23 to 25) the following important conclusion can be drawn: R_{hn} is incidental to the COD mass load ($Q.S_{ti}$), the sludge age (R_s) and the choice of the mean MLVSS concentration ($\bar{X}_v$) i.e. R_{hn} serves no basic kinetic function; it arises only as a consequence of the need for "diluting" the mass of sludge to a concentration that can be readily handled by the secondary settling tanks. The presence of inorganic solids in the sludge does not affect these conclusions; for a particular wastewater, this fraction can be included by a suitable choice of the MLVSS/MLSS ratio (f_i).

The process volume requirements for raw and settled wastewater per unit *raw* COD load follows from Eqs (23 and 24) i.e.

$$\frac{V_p}{(Q.S_{ti})} = \frac{R_s}{\bar{X}_t.f_i} \left\{ \frac{(1-f_{up}-f_{us})\ Y_h\ (1+fb_{hT}R_s)}{(1 + b_{hT}R_s)} + \frac{f_{up}}{P_v} \right\} (1-f_{rps}) \qquad (26)$$

where $\bar{X}_t$ = mean MLSS concentration in process

f_{rps} = fraction of COD removed by primary sedimentation

f_i = MLVSS/MLSS ratio (mgVSS/mgSS)

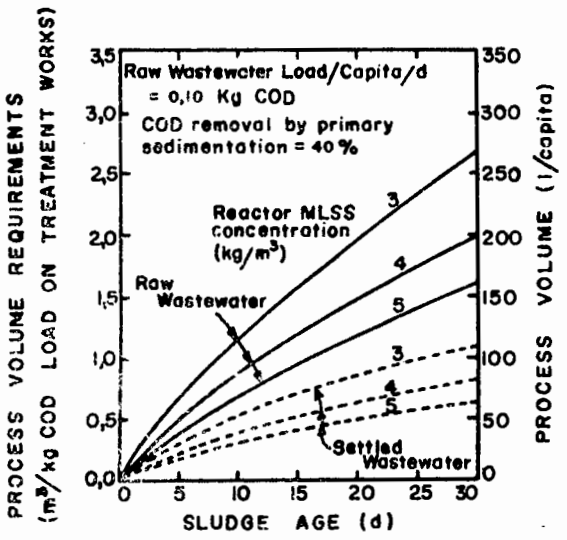

Fig 16 Process volume requirements in m^3/kgCOD raw wastewater load versus sludge age at different average process MLSS concentrations for raw and settled wastewater (assuming 40% COD removal by primary sedimentation). Process volume requirements in ℓ/capita also given based on a raw wastewater COD contribution of 0,10 kgCOD/capita/d

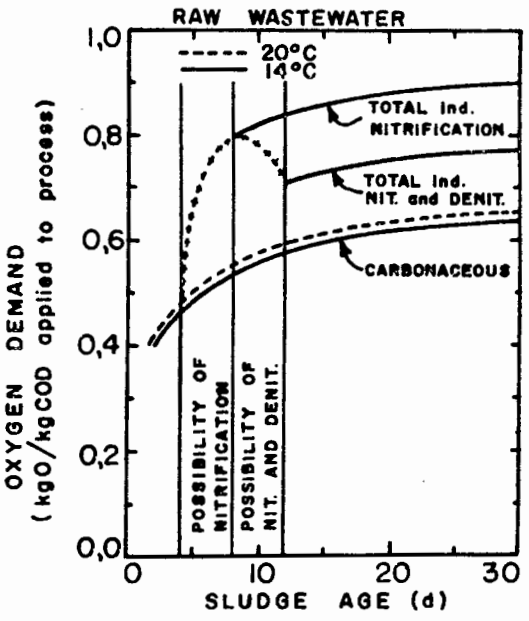

Fig 17 Carbonaceous, total including nitrification and total including nitrification and denitrification oxygen demand per unit COD load versus sludge age for raw wastewater (see Table 2).

In Fig 16 the process volume requirements in m^3/kg total raw COD load is shown versus R_s for the raw and settled wastewaters given in Table 2 for different concentrations of MLSS (in kg/m^3); primary sedimentation was assumed to remove 40% of the raw COD load (f_{rps} = 0,40) and the MLVSS/MLSS ratios of the sludges produced from raw and settled wastewaters are assumed to be 0,75 and 0,83 respectively. On the right hand side of Fig 16, the process volume requirements are given in *ℓ/capita* on the basis of a *raw* COD load per capita of 0,10 kgCOD/d. The process volume requirements per unit raw COD load increases as the sludge age increases and for settled wastewater the volume requirements are less than 50% of that required for raw wastewater i.e.for R_s = 25 days and $\bar{X}_t$ = 4 kg/m^3, 145 ℓ/capita process volume is required for raw wastewater but only 60 l/capita for settled wastewater. As sludge production increases slightly with decrease in temperature, the process volume requirements should be based on the lowest expected temperature T_{min}, but the difference between that at T_{min} and T_{max} is less than 5%.

Knowing the total volume of the process, the volumes of the reactors can be found for the different processes. For the Bardenpho, Phoredox and MLE processes (Figs 1 to 3) the fractional volumes of the total volume of the different reactors are equal to the sludge mass fractions e.g. if the anaerobic sludge mass fraction is 0,10, then the anaerobic reactor volume is a fraction 0,10 of the total volume. Also concentrations of sludge in all the reactors are equal to selected mean MLSS concentration $\bar{X}_t$.

In the UCT processes (Figs 5, 6 and 15) the sludge concentrations are not the same in the reactors so that the volume and sludge mass fractions are not equal. The volume fraction f_{va} and the sludge concentration X_{ta} in the anaerobic reactor are given by

$$f_{va} = f_{xa}\{(1 + r)/(r + f_{xa})\} \quad (27)$$

$$X_{ta} = \bar{X}_t . f_{xa}/f_{va} \quad (28)$$

The ratio of the volume fraction to the sludge mass fraction for the anoxic and aerobic reactors is given by

$$f_{vd}/f_{xd} = f_{vb}/f_{xb} = 1 - \{f_{xa}/(r + f_{xa})\} \quad (29)$$

where f_{vd} and f_{vb} are the volume fractions and f_{xd} and f_{xb} are the sludge mass fractions of the anoxic and aerobic reactors respectively. The sludge concentrations in the anoxic (X_{td}) and aerobic (X_{tb}) reactors are equal and are given by

$$X_{td} = X_{tb} = \bar{X}_t / [1-\{f_{xa}/(r + f_{xa})\}] \quad (30)$$

From Eq (30) it can be seen that the sludge concentrations in the anoxic and aerobic reactors are greater than the selected mean concentration $\bar{X}_t$. For r = 1 and f_{xa} = 0,15, X_{td} and X_{tb} are 15% higher than $\bar{X}_t$. The aerobic reactor sludge concentration X_{tb} is discharged to the secondary settling tanks. Consequently, the fact that in the UCT processes the feed sludge concentration to settling tanks is greater than the mean sludge concentration, must be taken into account in the design of the secondary settling tanks.

It should be noted that if the above procedure is used for calculating the volumes of the reactors in the Phoredox or UCT type processes, it will be found that for the same COD mass load, sludge age and temperature, the *total* volume of the UCT type processes is the same as that for a Phoredox process for the same *average* sludge concentration; however the sludge mass in the UCT type processes is not uniformly distributed which leads to a higher than average sludge concentration in the aerobic and anoxic reactors.

If in the UCT type processes, a certain selected sludge concentration must not be exceeded in the process to facilitate the design of the secondary settling tanks, the following alternative procedure can be used to calculate the volumes; if the anaerobic sludge mass fraction is f_{xa}, then the remaining sludge fraction $(1-f_{xa})$ is diluted into the anoxic and aerobic reactors at the specified concentration X_{tb} i.e. the volume of the anoxic and aerobic reactors is $(1-f_{xa}).MX_t/X_{tb}$. The subdivision of this volume into the correct anoxic and aerobic reactor volumes is easily found from the anoxic and aerobic sludge mass fractions because the sludge mass is uniformly distributed in these reactors of the process. Now the sludge concentration in the anaerobic reactor X_{ta} is a fraction $r/(1+r)$ of the concentration in the aerobic reactor X_{tb} i.e. $X_{ta} = X_{tb}\ r/(1+r)$. Knowing the mass of sludge in the anaerobic reactor i.e. $f_{xa}\ MX_t$ and the concentration, the volume of the anaerobic reactor is given by $f_{xa}\ MX_t/X_{ta}$. If the volume of the UCT type processes is calculated by this alternative method, it will be found that the volume of the UCT type process is greater than that of the corresponding Phoredox process (by about 15% for f_{xa} = 0,15) for the same aerobic reactor sludge concentrations.

(2) Total Oxygen Demand

The total oxygen demand in a nutrient removal process is the sum of that required for carbonaceous material (COD) degradation and nitrification less that recovered by denitrification.

The daily average carbonaceous oxygen demand (MO_c) is given by Marais and Ekama (1976):

$$MO_c = (S_{ti}.Q)(1-f_{us}-f_{up})\{(1-P_vY_h)+P_v(1-f)b_{hT}\ \frac{Y_hR_s}{(1+b_{hT}R_s)}\}(kgO/d) \quad (31)$$

The daily average nitrification oxygen demand is found from the mass of TKN converted to nitrate: for every mg TKN-N nitrified to nitrate, 4,57 mg O are required. The concentration of TKN per ℓ influent nitrified to nitrate is given by the nitrification capacity. Hence the nitrification oxygen demand is given by

$$MO_n = 4{,}57.N_c.Q \text{ (kg O/d)} \quad (32)$$

The oxygen recovered by denitrification is found from the mass of nitrate denitrified: for every mg NO_3-N denitrified, 2,86 mg O are recovered. The concentration of nitrate per ℓ influent denitrified is the difference between the nitrification capacity N_c and the effluent nitrate concentration N_{ne}. Hence the oxygen recovered by denitrification is given by

$$MO_d = 2{,}86.(N_c - N_{ne}).Q \text{ (kg O/d)} \quad (33)$$

Hence the average total mass of oxygen required per day in the aerobic sludge mass fraction of the process is given by:

$$MO_t = MO_c + MO_n - MO_d \text{ (kg O/d)} \quad (34)$$

The carbonaceous oxygen demand per unit COD load ($MO_c/(S_{ti}.Q)$, Eq (31) divided by $Q.S_{ti}$) versus sludge age R_s at 14°C and 20°C is shown in Fig 17 for the raw wastewater characteristics given in Table 2. From Fig 17 it can be seen that for R_s > 15 days, the increase in $MO_c/(S_{ti}.Q)$ with increase in R_s is marginal and that $MO_c/(S_{ti}.Q)$ is slightly higher at 20°C than at 14°C.

For a purely aerobic process, nitrification is likely for R_s > 4 days and is almost certain at R_s > 8 days for temperature above 14°C. For R_s > 8 days the nitrification oxygen demand per unit COD load ($MO_n/(S_{ti}.Q)$, Eq (32) divided by $Q.S_{ti}$) for the raw wastewater at 14°C is added to carbonaceous demand and also shown in Fig 17. Figure 17 shows that for the raw wastewater $MO_n/(Q.S_{ti})$ is about 40% of $MO_c/(Q.S_{ti})$ or about 28% of the combined total. These fractions depend largely on the influent TKN/COD ratio; the higher the ratio, the higher the proportion of MO_n with respect to MO_c.

For R_s > 12 days, denitrification becomes possible. The oxygen demand recovered by denitrification (assumed complete) per unit COD load ($MO_d/(S_{ti}.Q)$, Eq (33) divided by $Q.S_{ti}$) is deducted from the sum of the carbonaceous and nitrification oxygen demands for the raw wastewater at 14°C and the resulting total ($MO_t/(S_{ti}.Q)$ (i.e. Eq (34)) is shown on Fig 17. Figure 17 shows that with complete denitrification about 60% of the nitrification oxygen demand can be recovered. This demonstrates that in achieving high N removals, only about 20% more oxygen is required than for COD degradation only.

A plot similar to Fig 17 for raw wastewater also can be drawn for settled wastewater. In such a plot it will be found that for settled wastewater (i) $MO_c/(Q.S_t)$ is marginally higher than for raw wastewater - this is because a larger fraction of the total settled wastewater COD is biodegradable, (ii) $MO_n/(Q.S_{ti})$ is greater than that for raw wastewater - this is because the TKN/COD ratio for settled wastewater is higher than for raw wastewater (see Table 2); for settled wastewater $MO_n/(Q.S_{ti})$ is about 50% of $MO_c/(Q.S_{ti})$ or about 40% of the combined total, (iii) less oxygen can be recovered by denitrification because with the high TKN/COD ratio complete denitrification cannot be achieved; only about 40% of the nitrification oxygen demand can be recovered by denitrification.

Comparing the total oxygen demand for raw and settled wastewaters, a saving of about 30 to 40% in total oxygen demand (including denitrification) can be made by treating settled wastewater. This saving is possible because primary sedimentation reduces the COD load on the biological process by 35 to 45%.

Knowing the average total oxygen demand from Eqs (31 to 34) above, the peak total oxygen demand can be roughly estimated by means of a simple design rule. From a large number of simulations with the general dynamic model it was found that

provided the factor of safety on nitrification (S_f) is greater than 1,3, the relative amplitude {(Peak-average)/average} of the total oxygen demand is a fraction 0,50 of the relative amplitude of the total oxygen demand potential of the influent COD and TKN *load* $\{Q.(S_{ti} + 4,57.N_{ti})\}$. For example if the peak influent oxygen demand potential is obtained at a time of day when Q = 87,3 Mℓ/d, S_{ti} = 525 mgCOD/ℓ and N_{ti} = 49,9 mgN/ℓ and the average COD and TKN loads are 23200 kgCOD/d and 2540 kgN/d then the relative amplitude of the influent oxygen demand potential is 0,89; hence the relative amplitude of the total oxygen demand is roughly 0,50. 0,89 = 0,44; if the average total oxygen demand is 868 kgO/hr, then the peak total oxygen demand is approximately 1,44.868 = 1250 kgO/h. As with all simplified design rules, the above rule should be used with discretion and caution, and where possible, the peak total oxygen demand is best estimated by means of the general dynamic activated sludge model.

DISCUSSION

Process Selection

In the design of biological nutrient removal plants, the following broad guidelines can be given to assist in process type selection:

1) If the rapidly biodegradable COD concentration in the influent, S_{bsi}, is less than 60 mgCOD/ℓ (irrespective of the influent COD strength) excess P removal is unlikely to be achieved in any of the processes.

2) If S_{bsi} > 60 mgCOD/ℓ, excess P removal can be achieved provided nitrate can be excluded from the anaerobic reactor. Whether or not nitrate can be excluded from the anaerobic reactor depends on the influent TKN/COD ratio and the process type. The limits given below apply only where complete nitrification is obligatory - where complete nitrification is not obligatory, nitrate discharge to the anaerobic reactor can be avoided by limiting nitrification by, e.g. limiting the oxygen supply to the process, but such a strategy falls more in line with an emergency action than a design criterion.

   i) If the TKN/COD < 0,07 mgN/mgCOD, complete nitrate removal is possible and the Phoredox process is indicated.

   ii) If 0,07 < TKN/COD < 0,11 complete nitrate removal no longer is possible, but nitrate can be excluded from the anaerobic reactor by using the modified UCT process.

   iii) If 0,11 < TKN/COD < 0,14, the modified UCT process no longer can exclude nitrate from the anaerobic reactor and the UCT process is indicated provided the a-recycle ratio is carefully controlled. However, poor settling sludges may be encountered.

   iv) If TKN/COD > 0,14 it is unlikely that biological excess P removal will be achieved with normal municipal wasteflows.

Influent Strength

The ratio of the rapidly biodegradable COD concentration with respect to the total i.e. S_{bsi}/S_{ti} is approximately 0,20 for raw municipal wastewater (i.e. $f_{bs} \cong 0,24$) and approximately 0,30 for settled municipal wastewaters (f_{bs} = 0,33) (see Table 2). Consequently, the lower the influent COD strength (S_{ti}), the lower the S_{bsi}; when S_{ti} for raw wastewater is less than about 250 mgCOD/ℓ, S_{bsi} is about 50 mgCOD/ℓ and attainment of excess P removal for r or s-recycle ratios of 1:1 is unlikely or sporadic even if the process is correctly selected and optimally designed. Conversely, the higher the S_{ti}, the higher the S_{bsi} and the easier it is to establish the conditions for excess P removal and obtain high P fractions in the active mass (γ). As γ is a function of both (S_{bsa}-25) and the anaerobic sludge mass fraction f_{xa}, the adverse effect of low (S_{bsa}-25) at low S_{ti} can be countered to a degree by increasing f_{xa} to its maximum of 0,20. The following guidelines based on raw COD strengths are not unreasonable for an initial estimate of f_{xa} to obtain optimal P removals: S_{ti} < 400 mgCOD/ℓ, f_{xa} = 0,20; 400 < S_{ti} < 700, f_{xa} = 0,15; S_{ti} > 700,

f_{xa} = 0,10. The initial estimates must be modified depending on the influent P/COD ratio and the S_{bsi} concentration.

Influent Rapidly Biodegradable COD concentration and TKN/COD ratio

1) The crucial importance of the influent rapidly biodegradable COD concentration (S_{bsi}) on excess P removal makes it important to avoid those conditions that can reduce S_{bsi}, e.g.

   i) Hydraulic jumps, cascades, aerated grit channels raise the D.O. of the influent and lead to utilization of S_{bsi} in the anaerobic reactor.

   ii) Open Archimedian screw pumps also entrain D.O. into the influent and recycle flows.

   iii) Septic tanks in the sewer system discharge effluents devoid of S_{bsi} and with a high TKN/COD ratio. Septic tanks should be taken out of commission and the domestic wastewater discharged direct to the sewerage system.

   iv) Stormwater ingress and groundwater infiltration into the sewerage system dilute the wastewater strength and hence also S_{bsi}.

2) Wastewater characteristics favourable for high biological P and N removals are low TKN/COD and P/COD ratios, high COD strengths and rapidly biodegradable COD concentrations, and high maximum specific growth rates of the nitrifiers at 20°C (μ_{nm20}). Consequently when framing industrial effluent policies, cognizance should be taken of the effects of industrial discharges on the municipal wastewater characteristics. For example, brewery wastewaters have very low TKN/COD ratios, gas-works wastewaters have high TKN/COD ratios and metal finishing industry wastewaters contain heavy metals which may cause a significant reduction in the μ_{nm20} value.

Inplant D.O. Control

Unless the D.O. is controlled to remain in the range 1,5 to 3,0 mgO/ℓ, the P removal can be adversely affected: If too high, denitrification will be reduced, especially in the small first anoxic reactor of the modified UCT process, causing nitrate to be discharged to the anaerobic reactor. If too low, the P removal may be reduced due to incomplete uptake in the aerobic reactor, or nitrification will be adversely affected and poor settling sludges may develop. In P removal plants, even if optimally designed, failure in the requirement for close oxygen control is likely to be one of the main causes for poor or erratic P removal performance. The problem of proper D.O. control is a severe one particularly under cyclic flow and load conditions in small plants; the present reliability and stability of monitoring instruments is poor, so that inplant D.O. control normally is manual and relies heavily on operator judgement. Under equalized flow and load conditions, manual D.O. control is feasible and the only monitoring equipment required is a manually operated D.O. meter. Flow and load equalization is now readily achievable by installing an equalization tank upstream of the plant and operating it by a micro-computer based control strategy to give optimal equalization of both flow and load. The continuous monitoring equipment required is of a simple, reliable and stable kind involving only liquid level measurements. The modern microcomputer likewise is reliable, and inexpensive and should not be a cause for apprehension, even when installed on small works (Dold, Buhr and Marais, 1982).

In the operation of the equalization tank, a factor of crucial importance with unstirred tanks (mixing by aeration to be avoided) is to design and operate the tank such that the solids that settle during the day are flushed out eacy day. If this precaution is not heeded, a sludge layer will accumulate and remova a significant fraction of the S_{bsi} by fermentation (Nicholls and Marais, 1982).

Sludge Disposal Practices

1) When the anaerobic digestor cannot accommodate the thickened waste activated sludge, often the sludge is discharged to a point prior to the primary settling tanks. This practice can cause a significant reduction in S_{bsi} particularly if the influent flow is lifted by Archimedian screw pumps to the inlet works. Such excess waste sludge should be returned to the aerobic reactor.

2) Avoid discharge of waste activated sludge to the sewerage system for sludge handling at another wastewater treatment facility lower down the sewer line. This practice can cause a significant reduction in S_{bsi}.

Solid Waste Practices

In South Africa, garbage grinding and disposal to sewers is not common. Whenever garbage grinding is practised, the fraction of unbiodegradable particulate COD (f_{up}) will be higher than the 0,13 value accepted in this paper. From an analysis of data reported in Canada (Sutton *et al.* 1979), van Haandel and Marais (1981) found that f_{up} = 0,25. For such high f_{up} values, the TKN/COD ratio guidelines for process selection given in this paper have to be reduced by about 0,05 mgN/mgCOD. Caution should be exercised in the selection of the f_{up} value; its magnitude has important implications throughout the design calculations, in particular, it has a strong influence on the process volume requirements and total oxygen demand.

CONCLUSIONS

1. The average influent wastewater characteristics -

   (i) COD concentration
   (ii) TKN/COD concentration ratio
   (iii) rapidly biodegradable COD fraction (f_{bs})
   (iv) maximum specific growth rate of the nitrifiers at 20°C (μ_{nm20})
   (v) maximum and minimum temperatures (T_{max} and T_{min})
   (vi) P/COD concentration ratio

govern the design of and the effluent quality attainable in the activated sludge process for P and N removal.

2. Once the sludge age of a selected process is fixed the removals of N and P also are fixed and the N and P removal *efficiencies* depend on the TKN/COD and P/COD ratios of the wastewater. Because complete denitrification can be achieved only for TKN/COD ratios < 0,08 mgN/mgCOD, the higher the ratio above 0,08 mgN/mgCOD, the lower the N removal efficiency.

3. Attainment of excess P removal is crucially dependent on the rapidly biodegradable COD concentration in the influent S_{bsi}. For recycle ratios to the anaerobic reactor of 1:1, if S_{bsi} < 50 mgCOD/ℓ, it is highly unlikely that excess P removal can be achieved in any process. If S_{bsi} > 50 mgCOD/ℓ, excess P removal can be achieved provided nitrate can be excluded from the anaerobic reactor, in which event the degree of excess P removal depends on the magnitude of S_{bsi} above 50 mgCOD/ℓ and the total influent COD strength (S_{ti})

4. In general, the establishment of a rapidly biodegradable COD concentration in the anaerobic reactor (S_{bsa}) in excess of 25 mgCOD/ℓ, to stimulate excess P removal, becomes increasingly more difficult as the raw influent COD strength of the wastewater (S_{ti}) decreases: For average rapidly biodegradable COD fractions ranging between 0,20 to 0,25, the minimum S_{ti} for which S_{bsa} is greater than 25 mgCOD/ℓ is about 250 mgCOD/ℓ; as S_{ti} increases above 250 mgCOD/ℓ, the establishment of S_{bsa} greater than 25 mgCOD/ℓ becomes increasingly easier and the excess P removal per unit influent COD increases and the attainment of excess P removal becomes less sensitive to external factors, e.g. D.O. control in the process.

5. For successful excess P removal in the Phoredox process, complete denitrification must be achieved to avoid nitrate discharge to the anaerobic reactor. Complete denitrification can be achieved only for TKN/COD ratios < 0,08 mgN/mgCOD.

6. For TKN/COD ratios > 0,08 mgN/mgCOD, complete denitrification cannot be achieved and the only viable processes for obtaining excess P removal are the UCT type processes.

7. In the UCT type processes, by appropriate control of the mixed liquor a-recycle,

the anaerobic reactor always can be protected against nitrate discharge for TKN/COD ratios up to 0,14 mgN/mgCOD even though nitrate will be present in the effluent. For TKN/COD ratios < 0,11, the modified UCT process can achieve excess P removal and has the advantage over the UCT process of less need for operator intervention and is more likely to maintain reasonably good sludge settling characteristics. For TKN/COD ratios > 0,11 mgN/mgCOD, the only process that can achieve excess P removal is the UCT process, but it is likely that rather poor sludge settling characteristics will be obtained if the influent COD is high.

8. For TKN/COD ratios > 0,14 mgN/mgCOD, it is unlikely that biological excess P removal can be obtained when complete nitrification is obligatory due to the inability to achieve sufficient denitrification. However, such high TKN/COD ratios are unlikely to be encountered in raw or settled municipal wastewaters.

9. If there is any uncertainty regarding the influent wastewater characteristics, the Phoredox process *must not be selected.* In this process, if the actual wastewater characteristics are unfavourable with respect to those assumed in the design, the process may fail completely in its excess P removal objective. Under these circumstances, the modified UCT/UCT process combination (i.e. option of r-recycle to be abstrated from the 1st or 2nd anoxic reactor) is the indicated process.

10. Primary sedimentation is unfavourable for achieving high removals of both N and P because it significantly increases the TKN/COD and P/COD ratios and significantly reduces the COD strength of the wastewater although the rapidly biodegradable COD concentration is only marginally affected. However, primary sedimentation significantly reduces the process volume requirements and total oxygen demand.

ACKNOWLEDGEMENT

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LIST OF SYMBOLS

a = mixed liquor recycle ratio from the aerobic to the anoxic reactors. Subscript o denotes optimum

b_{hT} = endogenous mass loss rate for heterotrophic organisms at T°C (/d)
= $b_{h20}(1,029)^{(T-20)}$

b_{h20} = the rate at 20°C = 0,24/d

b_{nT} = endogenous respiration rate for nitrifying bacteria at T°C (/d)
= $b_{n20}(1,029)^{(T-20)}$

b_{n20} = the rate at 20°C = 0,04/d

D_p = denitrification potential (mgN/ℓ influent). Additional subscripts 1, 3 and p refer respectively to primary and secondary anoxic reactors, and process total.

d = dissolved oxygen concentration (mgO/ℓ). Subscripts a, r and s refer to the concentrations in the a, r and s-recycles respectively.

f = unbiodegradable fraction of active mass
= 0,20 mgVSS/mgVSS

f_{bs} = fraction of biodegradable influent COD which is rapidly biodegradable.

f_i = MLVSS to MLSS concentration ratio of the mixed liquor.

f_n = nitrogen fraction of the MLVSS (mgN/mgVSS) = 0,10 mgN/mgVSS

f_p = phosphorus fraction of the inert MLVSS

= 0,015 mgP/mgVSS

f_{rps} = fraction of raw total COD removed by primary sedimentation

f_u = unbiodegradable COD fractions in the influent (mgCOD/mgCOD). Additional subscripts p and s refer respectively to particulate and soluble fractions

f_v^* = general parameter for volume fractions

f_x^* = general parameter for sludge mass fractions

*Additional subscripts a, b, d, 1, 3 and m refer respectively to anaerobic, total aerobic, total anoxic, primary anoxic, secondary anoxic and maximum unaerated allowable. Subscripts t and m following d refer respectively to total required for complete denitrification and maximum allowable. Subscript min following 1 and 3 refers to minimum values. Subscripts 1 and 2 following subscript d refers respectively to the first and second anoxic reactors in a modified UCT process.

K = general parameter for denitrification rate (mgNO_3-N/mgVASS/d). Subscripts 1 and 2 refer respectively to the 1st and 2nd rates in the primary anoxic and 3 to the rate in the secondary anoxic. Additional subscripts T and 20 refer to T°C and 20°C respectively

M = prefix denoting mass

N_c = nitrification capacity per unit influent flow (mgN/ℓ)

N_n = nitrate concentration (mgN/ℓ). Additional subscripts e, r and s refer respectively to effluent, r and s-recycle concentrations.

N_s = nitrogen required for sludge production (mgN/ℓ influent flow)

N_t = TKN concentration (mgN/ℓ). Additional subscripts e and i refer to effluent and influent respectively

O = general parameter for oxygen consumption rate (mass/d). Subscripts c, d, n and t refer respectively to that for carbonaceous material degradation, recovered by denitrification, nitrification and total

P_f = excess phosphorus removal propensity factor (mgCOD/ℓ)

P_s = phosphorus in daily sludge wastage per ℓ influent flow (mgP/ℓ) i.e. the phosphorus removal from the wastewater

P_t = total phosphorus concentration (mgP/ℓ). Additional subscripts i and e refer respectively to influent and effluent

P_v = COD to VSS ratio of the sludge mass = 1,48 mgCOD/mgVSS

Q = daily influent flow rate (ℓ/d)

R_{hn} = process nominal retention time (d)

R_s = sludge age (d)

r = mixed liquor recycle ratio from the anoxic to the anaerobic reactor in the UCT type processes

s = underflow recycle ratio

S_f = factor of safety for ensuring nitrification

S_{ti} = total influent COD concentration (mgCOD/ℓ)

S_{bi} = biodegradable influent COD concentration (mgCOD/ℓ)

= $(1-f_{us}-f_{up}).S_{ti}$

S_{bsi} = rapidly biodegradable soluble influent COD

S_{bsa} = rapidly biodegradable COD concentration in the anaerobic reactor (mgCOD/ℓ)

ΔS_{bs} = rapidly biodegradable COD utilized in anaerobic reactor due to nitrate and dissolved oxygen discharged to it

T = temperature at °C. Subscripts max and min refer to maximum and minimum values

V_p = process volume (ℓ)

X = general parameter for sludge concentration (mgVSS/ℓ). Subscripts a, e, i, v and t refer respectively to active, endogenous, inert, volatile (MLVSS) and total (MLSS) concentration. Additional subscripts a, b and d following subscript t refer respectively to anaerobic, aerobic and anoxic concentrations

$\bar{X}$ = weighted average sludge concentration in process (mg/ℓ). Subscripts v and t refers to MLVSS and MLSS respectively

Y_h = yield coefficient = 0,45 mgVSS/mgCOD

μ_{nm} = maximum specific growth rate of the nitrifiers. Additional subscript T or 20 refers to T°C or 20°C respectively

γ = coefficient of excess P removal i.e. P content of active mass (mgP/mgVASS)

REFERENCES

Arkley, M. and G.v.R.Marais (1982). Effect of the anoxic sludge mass fraction on the activated sludge process. Research Report No. W 38, Dept. of Civil Eng., Univ. of Cape Town.

Dold, P.L., G.A.Ekama and G.v.R.Marais (1980). A general model for the activated sludge process. Prog.Wat.Tech., 12, 47-77.

Dold, P.L., H.O.Buhr and G.v.R.Marais (1982). Design and control of equalization tanks. Research Report No. W 42, Dept. of Civil Eng., Univ. of Cape Town.

Marais, G.v.R. and G.A.Ekama (1976). The activated sludge process Part I - steady state behaviour. Water S.A., 2, 4, 163-200.

Marais, G.v.R., I.P.Siebritz and G.A. Ekama (1982). Review: Observations supporting phosphorus removal by biological uptake. Presented at I.A.W.P.R. post conference seminar on phosphate removal, Pretoria. Procs. to be published in Water Science and Technology.

Martin, K.A.C. and G.v.R. Marais (1975). Kinetics of enhanced phosphorus removal in the activated sludge process. Research Report No. W 14, Department of Civil Eng., Univ. of Cape Town.

Nicholls, H.A. and G.v.R.Marais (1982). Performance of large scale nutrient removal activated sludge plants. Research Report No. W 43, Dept. of Civil Eng., Univ. of Cape Town.

Sehayek, E. and G.v.R. Marais (1981). Kinetics of biological nitrogen removal in the single sludge activated sludge process. Research Report No W 41, Dept. of Civil Eng., Univ. of Cape Town.

Siebritz, I.P., G.A.Ekama and G.v.R.Marais (1982). A parametric model for biological excess phosphorus removal. Presented at the I.A.W.P.R. post conference seminar on phosphate removal, Pretoria. Procs. to be published in Water Science and Technology.

Sutton, P.M., B.E.Jank, B.A. Monaghan and K.L.Murphy (1979). Single sludge nitrogen removal systems. Research Report No 88, Water Technology Centre, Burlington, Canada.

van Haandel, A.C. and G.v.R.Marais (1981). Nitrification and denitrification in the activated sludge process. Research Report No W 39, Dept. of Civil Eng., Univ. of Cape Town.

van Haandel, A.C., G.A.Ekama and G.v.R.Marais (1981). The activated sludge process Part 3 - single sludge denitrification. Water Research, 15, 1135-1152.

van Haandel, A.C., P.L.Dold and G.v.R.Marais (1982). Optimization of Nitrogen removal in the single sludge activated sludge process. Presented at 11th IAWPR Conf. Cape Town. To be published in Water, Science and Technology.

WATER RESEARCH COMMISSION OF SOUTH AFRICA

THEORY, DESIGN AND OPERATION OF NUTRIENT REMOVAL ACTIVATED SLUDGE PROCESSES

(FINAL DRAFT)

TECHNOLOGICAL TRANSFER PUBLICATION TO BE PUBLISHED IN 1983

THEORY, DESIGN AND OPERATION OF NUTRIENT REMOVAL ACTIVATED SLUDGE PROCESSES

FOREWORD

In the Republic of South Africa the point of maximum economic exploitation of conventional water resources is rapidly approaching. In addition, the country is also faced with deteriorating water quality which may become a limiting factor in water resources development prior to limitations on water quantity.

The accelerated deterioration of water quality is a result of, amongst others, the discharge of ever increasing quantities of treated effluents to our rivers and streams. Effective removal of pollutants from wastewaters, particularly the nutrients carbon, nitrogen and phosphorus, therefore, is of the utmost importance. Furthermore, high quality effluents may serve as an economic source to augment our dwindling water resources.

The need for pollution control and indirect reuse of treated wastewater is legally expressed in the Water Act 54 of 1956 and standards promulgated in terms of the act. In the General and Special Standards which were promulgated in 1962, the emphasis fell on adequate removal of carbonaceous material and the transformation of ammonia to nitrate. More recently accelerated eutrophication of many of South Africa's impoundments, with attendant health, water quality and aesthetic problems, has become apparent and resulted in the promulgation in 1980 of an upper limit for effluent phosphates for a number of critical catchments. Furthermore, limiting the total dissolved solids content of treated effluents now is also considered of prime importance. The need to remove the nutrients *and* reduce the increase of the dissolved solids during treatment, places difficult demands on future waste water treatment plants.

Technology for the removal of the nutrients nitrogen and phosphorus from waste water has been developed to a high level in the Republic of South Africa. Many organizations have been instrumental in this development, including research organizations, engineering consulting firms and local authorities. A wide range of physical, chemical and biological processes and combinations of these, are now available both for upgrading of existing works and design of new works. Methods available are: Physical-chemical, of

particular use for removal of phosphates from the effluents of existing works - the only viable option, in fact, for dealing with trickling filter effluents; physical-chemical-biological,* for the removal of nitrogen and phosphorus, of use where the characteristics of the wastewater are unfavourable for the biological removal of the nutrients; biological,** for the removal of all or major fractions of the nitrogen and phosphorus in the influent; no, or only minimal addition of chemicals is needed to produce the required effluent phosphate quality. Biological nutrient removal is particularly attractive for the treatment of municipal wastewaters because, treatment costs are generally less than with physical-chemical methods, the salt concentration of the effluent is not raised as with chemical addition and the characteristics of the wastewater usually are amenable to this type of treatment. In consequence, the Water Research Commission has been greatly interested in developing this method of nutrient removal.

The Water Research Commission has stimulated, co-ordinated and financed research and development work in the field of biological nutrient removal inthe activated sludge process from about 1973. Since that time it has contracted the National Institute for Water Research of the Council for Scientific and Industrial Research, the Universities of Cape Town and Pretoria and the City Council of Johannesburg to do research and development work in this field on a co-ordinated joint venture basis. A significant amount of information on processes for biological nutrient removal is now available. Much of this information has already been published in local and international journals as well as having been presented at a number of conferences, seminars and open days. However, in the light of the urgent need of local authorities and others who have to meet ever stricter effluent standards, and in particular the effluent phosphate

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*Phosphorus removal by chemical addition, the reader is referred to the Water Research Commission publication "Guidelines for chemical removal of phosphorus from municipal effluents."

**For example, the LFB process - see

standard of 1 mg/ℓ soluble orthophosphate which is to be strictly enforced in a number of critical catchments as from August 1985, it was decided to compile a comprehensive information document on the biological removal of nitrogen and phosphorus covering relevant results and findings made under Water Research Commission sponsored projects.

This publication has been compiled as a self-contained document which does not require reference to other publications on wastewater treatment. It is intended primarily for the design engineer and management staff responsible for operation and control of wastewater purification works. The level of presentation assumes that the reader has had tertiary training and/or considerable practical experience in the field of wastewater treatment.

The basic process for the simultaneous biological removal of phosphorus and nitrogen was proposed by Barnard in 1976 and is called the Phoredox process in South Africa, and the Bardenpho$^{(R)}$* or Modified Bardenpho in the United States. This process belongs to the single sludge, multi reactor group of processes. For the phosphorus removal aspect the fundamental principle embodied in this process is that an anaerobic state needs to be created at some point in the process such that phosphate is released, a consequence of which induces biological uptake of phosphate in excess of normal metabolic requirements when the sludge is aerated subsequently. In the Phoredox process the endeavour is to create the requisite anaerobic state by mixing the influent waste stream with the sludge recycled from the secondary settling tank without aeration in an anaerobic tank at the head of the works.

This method for promoting the anaerobic state appears in a number of processes that developed from the Phoredox process in order to accommodate waste waters with unfavourable characteristics

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*The Bardenpho$^{(R)}$ process is a patented process. Greater details on the process and its application for site specific conditions can be obtained by arrangement with the patent holders, Messrs SAIDCOR, at P O Box 395, Pretoria, RSA, 0001.

or in which nitrification-denitrification is not required. One such development, known as the UCT process is described in detail in this puboication. Other processes which also incorporate the Phoredox principle, are not dealt with; for example, the AO process (basically a simplified Phoredox process) is not considered since this process is designed to remove phosphate in short sludge age systems where nitrification is prevented from occurring, and is unlikely to find significant application in the RSA. The process developed by Roberts and Kerdachi at Pinetown, Natal, also is not dealt with. This process differs from the others in that nitrification, denitrification and the anaerobic state, to induce P release, all take place in one reactor. Also, the process is oxygen limited, in consequence, its biological response with regard to sludge production, oxygen demand, nitrification, etc. is not amenable to description by the kinetic models governing non-oxygen limited processes such as the multi reactor Phoredox, UCT and AO processes. The writers of this manuscript felt therefore that the Robert-Kerdachi process falls outside their ambit of competence.

All the above processes are of the main stream kind. Side stream processes, of which the Phostrip process is currently the most widely used, are not discussed in this publication. In side stream processes the anaerobic state is created by passing a fraction of the secondary settler underflow through an anaerobic reactor to release phosphates through endogenous respiration (instead of by the addition of feed waste flow) and precipitating the released phosphates by lime addition. Insufficient data on the behaviour of this process was available to the authors to allow directives to be put forward for design and operation of this process for producing effluents complying with South African effluent regulations with regard to both nitrogen and phosphorus.

Guidelines for design set out in this publication are based primarily on about ten years of extensive laboratory investigations at the University of Cape Town on biological nutrient removal from predominantly domestic wastewaters. These guidelines were verified on data generated at pilot scale on the National Institute for Water

Research's facility at Daspoort, Pretoria and at full-scale on the Johannesburg Goudkoppies and Northern Works. The mathematical model for carbonaceous material oxidation, nitrification and denitrification have been shown to give accurate predictions of full scale plant response. The theory for biological phosphate removal is currently still in a development stage with research in this area continuing. Nonetheless, tentative but conservative guidelines for process selection and design for the biological phosphate removal aspect are presented.

Biological nutrient removal in the activated sludge process has only a short history of application. Currently in South Africa there are of the order of thirty plants designed for and being operated to obtain biological nutrient removal, with varying degrees of success. Practical experience on these plants should increase knowledge on the application of the process to a variety of wastewaters under different operating conditions and effluent requirements. Further research is still needed and is continuing in a number of areas where knowledge is still inadequate, for example, the mechanism(s) and factors controlling excess phosphate removal, the role of the anaerobic stage in the process, settling characteristics of the sludge formed in the process and factors which control these, as well as scum formation. This publication therefore does not pretend to be the final word on biological nutrient removal, it is an information document with interim guidelines for design and operation of biological nutrient removal plants.

Chairman
Water Research Commission

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by G A Ekama and G v R Marais

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by G A Ekama and G v R Marais

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by G A Ekama and G v R Marais

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by G A Ekama and G v R Marais

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ABSTRACT

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by G A Ekama, G v R Marais and I P Siebritz

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ABSTRACT

The evolution of a quantitative parametric model for biological excess phosphorus removal is described and it is shown that the readily biodegradable COD fraction of the influent is one of the most important parameters in excess P removal. The equations of the model, which allow prediction of the magnitude of excess P removal in terms of the process design parameters and wastewater characteristics, are presented together with their capabilities and limitations. The design procedure is critically discussed in the light of recent research findings in the biological excess P removal field. The implications of the model on nutrient removal process design is described. Step by step design procedures for the different nutrient removal processes are set out and a design chart by means of which the excess P removal can be rapidly estimated is presented. Rough guidelines for process selection and anaerobic reactor sizing based on wastewater characteristics are set out. The design procedures are demonstrated with the aid of worked examples for raw and settled wastewaters.

CHAPTER EIGHT SECONDARY SETTLING TANKS

by G A Ekama*, A R Pitman**, M Smollen*** and G v R Marais*

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ABSTRACT

Settling behaviour of mixed liquor as described by the stirred batch settling test is discussed. Batch settling test data are then integrated with secondary settling tank behaviour via the flux theory using both graphical and analytical procedures. A secondary settling tank design and operating chart is presented and its use demonstrated by worked examples. Practical aspects of secondary settling tank design are discussed.

CHAPTER ONE

FUNDAMENTALS OF BIOLOGICAL BEHAVIOUR

G v R Marais and G A Ekama

1. INTRODUCTION

Life, in order to persist, requires a continuous throughput of (1) matter and (2) energy:

(1) The most prominent elements passing through the life system are hydrogen (H), oxygen (O), carbon (C), nitrogen (N), phosphorus (P) and sulphur (S), plus a host of minor elements.

(2) Energy is derived principally from three sources and these form a convenient criterion to categorise the organisms implicated:

(a) Solar radiation : photo-synthetic autotrophs
(b) Organic compounds : heterotrophs
(c) Inorganic compounds : chemical autotrophs.

(a) In the biosphere the fundamental source of energy is solar radiation. The photo-synthetic autotrophic cells fix a small fraction of the solar energy by forming complex high energy organic (H,C,O) compounds and producing oxygen. Of the matter requirements the elements H and O are obtained from H_2O; carbon from CO_2 and phosphorus, nitrogen and sulphur from the dissolved salts of these elements. Both H_2O and CO_2 are readily available; sulphur is usually in adequate supply; however the availability of phosphorus and nitrogen usually is limited - phosphorus does not occur readily in soluble form and nitrogen is useful to the organism principally in the NH_4^+ and NO_3^- forms. The restricted availability of these two elements usually constitute the limiting factors to the mass of autotrophic life a body of water can generate. For this reason, phosphorus and nitrogen are termed eutrophic (life-giving) substances. Phosphorus is limited by the mass available or entering a particular ecosystem, but ammonia can be generated from dissolved molecular nitrogen by certain micro-organisms. In

this respect the control of phosphorus in a body of water takes on a greater significance than the control of nitrogen.

Whereas the eutrophic elements N and P normally are the principal agents of pollution in bodies of water, by stimulating autotrophic growth, the action associated with this growth, of producing oxygen, is utilized in the Oxidation Pond system of wastewater treatment - the oxygen is utilized by heterotrophic organisms to metabolize the carbonaceous material in the influent to the pond, in this fashion to assist in destroying organic energy, as described in (b) below.

(b) The high energy organic compounds synthesized by the autotrophs forms the basic source of energy for the heterotrophic cells to synthesize the more complex molecules that constitute the cell mass, including proteins. Only a fraction of the energy utilized is incorporated in the cell mass generated, the balance is lost as heat. The mass of organisms thus generated in turn forms the matter and energy sources (prey) for other organisms that live on them (predators), and these in turn become prey to yet other predators. Each prey-predator transformation is accompanied by a substantial loss of energy; in this fashion through the sequential chain of life there is a continuous reduction of the organically bound energy originally fixed by the photo-synthetic autotrophs. When the organic energy reduces to zero heterotrophic life ceases. In waste water treatment plants the full chain of life does not develop so that a substantial fraction of the input energy is retained in the life mass in the system but this fraction is physically separated from the liquid in the sludge wasted daily (for further treatment) leaving very little organic energy in the effluent.

(c) Chemical autotrophs derive their energy for growth from the oxidation of inorganic compounds. In wastewater microbiology the principal species of interest in this genera are the nitrifying bacteria. These bacteria are obligate aerobes (i.e. can grow only when oxygen is present), and derive energy by oxidixing saline ammonia, to nitrite and nitrate. In wastewater treatment the

nitrifyers form a vital link in the removal of the autotrophic element nitrogen from the water by converting ammonia nitrogen to nitrate nitrogen when, by appropriate design, the heterotrophs can be forced to utilize the nitrate in the heterotrophic metabolism of carbonaceous material, in which action the nitrate is reduced to molecular nitrogen and escapes as nitrogen gas. (see later)

1.1 Objectives of Wastewater Treatment

From the considerations above the objectives of wastewater treatment are seen to be twofold:

1. Reduction of organic-bound energy in the waste flow to a level where it can sustain only minimal heterotrophic growth, and

2. Reduction of the autotrophic substances, phosphates, ammonia and nitrates, to levels where the photo-synthetic autotrophic micro-organisms are severely limited in their growth, and therefore in their capacity to fix solar energy as organic energy in the body of receiving water.

2. BIOLOGICAL BEHAVIOUR

Biological metabolism is principally a process of energy conversion. In biological wastewater treatment processes, the input energies are present in the wastewater in the form of carbonaceous and nitrogenous organic compounds. These are converted into other energy forms during which some of the energy is lost as heat.

The carbonaceous energy is utilized by the heterotrophic group of micro-organisms. This is a wide spectrum group, which, given sufficient time and appropriate environmental conditions, will utilize virtually every type of organic material. The group is ubiquitous and in any given situation those members of the group that obtain maximum benefit from the specific organic material and environmental conditions will develop. As the organic source or the environmental conditions change, so associated changes in the heterotrophic organisms species take place.

The nitrogenous material serves as an energy source only in the free and saline ammonia form. Proteinaceous nitrogen is broken down into its ammoniacal and carbonaceous constituents by heterotrophs. The free and saline ammonia is utilized as an energy source by two specific organisms species, the *Nitrosomonas* and *Nitrobacter*. The

former converts ammonia to nitrite and the latter nitrite to nitrate, these two organism species jointly being called the nitrifiers. Compared to most of the members of the heterotrophic group, the nitrifiers are slow growing. Because the group consists of only two species, each performing a particular function in the nitrification process, the environmental conditions must be conducive to both species, otherwise one or the other will not propagate and nitrification will be adversely affected. In general the environmental conditions for the nitrifiers are much more circumscribed than those for the heterotrophs. With the heterotrophs, the variety of organisms is so large that some group of the species nearly always will adapt to the biodegradable organic material in the influent or changes in the environmental conditons. With the nitrifiers, once the environmental conditions change to beyond a rather restricted range, they cease to grow.

2.1 Electron Donors and Acceptors

For all the organisms the energy source serves two functions:

(1) for the supply of material which is transformed to new cell material i.e. synthesis of new cell mass,

(2) for the supply of energy to effect this transformation.

For heterotrophic growth,energy is obtained from the carbonaceous material, as follows: Each organic molecule is split to give hydrogen ions, carbon dioxide molecules and electrons. Because it releases electrons the organic molecule is called an *electron donor* and on yielding electrons the molecule is said to be *oxidized.* The electrons (and hydrogen ions) are eventually transferred to a molecule that can receive them and this molecule is called an *electron acceptor;* on receipt of electrons the molecule is said to be *reduced.* In this oxidation-reduction (redox) reaction *free energy* is released, that is, energy that can be utilized to do work.

Under *aerobic* conditions the electron acceptor is oxygen (O_2) and it is reduced to water (H_2O). If no oxygen is

available but nitrate (NO_3^-) or nitrite (NO_2^-) is, an *anoxic* state exists; the NO_3^- and NO_2^- serve as electron acceptors and both are reduced to nitrogen gas and water. If no O_2, NO_2^- or NO_3^- is present an *anaerobic* state exists and the organism generates its own electron acceptor internally (endogenously), in contrast to externally provided (exogenous) electron acceptors (O_2, NO_2^- and NO_3^-), in the aerobic and anoxic states.*

The quantity of free energy released in a redox reaction depends on the electron donor and the acceptor. When carbonaceous material is the donor and oxygen is the final acceptor the free energy is relatively high; with NO_2^- and NO_3^- as acceptor the free energy is about 5% less than with oxygen (McCarty, 1964). Internally generated electron acceptors give rise to redox reactions that yield very little free energy.

Taking oxygen as the electron acceptor the free energy per electron transferred for different configurations of carbonaceous molecules lies within a relatively narrow band of values. For sewage which contains an innumerable number of different carbonaceous substances, the mean free energy per electron transferred is virtually constant, McCarty (1964).

In aerobic synthesis of organism mass a *fraction* of the carbonaceous material (with oxygen as electron acceptor) is oxidized via a complex set of redox reactions, to yield free energy, see Fig 1.1. The free energy (via ADP-ATP exchanges) is utilized to reorganize the remaining fraction of carbonaceous material into proto-plasmic

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*In Bacteriology if the final hydrogen ion and electron acceptor is molecular dissolved oxygen, then the process of substrate oxidation is termed aerobic; if it is chemically bound oxygen, i.e. nitrate, nitrite or sulphate, the process is termed anaerobic; if the hydrogen ion and electron acceptors originate outside the cell, i.e. exogenous, the whole process is termed one of respiration;

if the terminal electron acceptors originate inside the cell, i.e. endogenous, the process is called fermentation. In Sanitary Engineering, the usage of some of these terms differs from that in Bacteriology. In particular if no dissolved oxygen is present, the process or environment is called anoxic, if neither dissolved oxygen nor nitrate is present, the process or environment is called anaerobic.

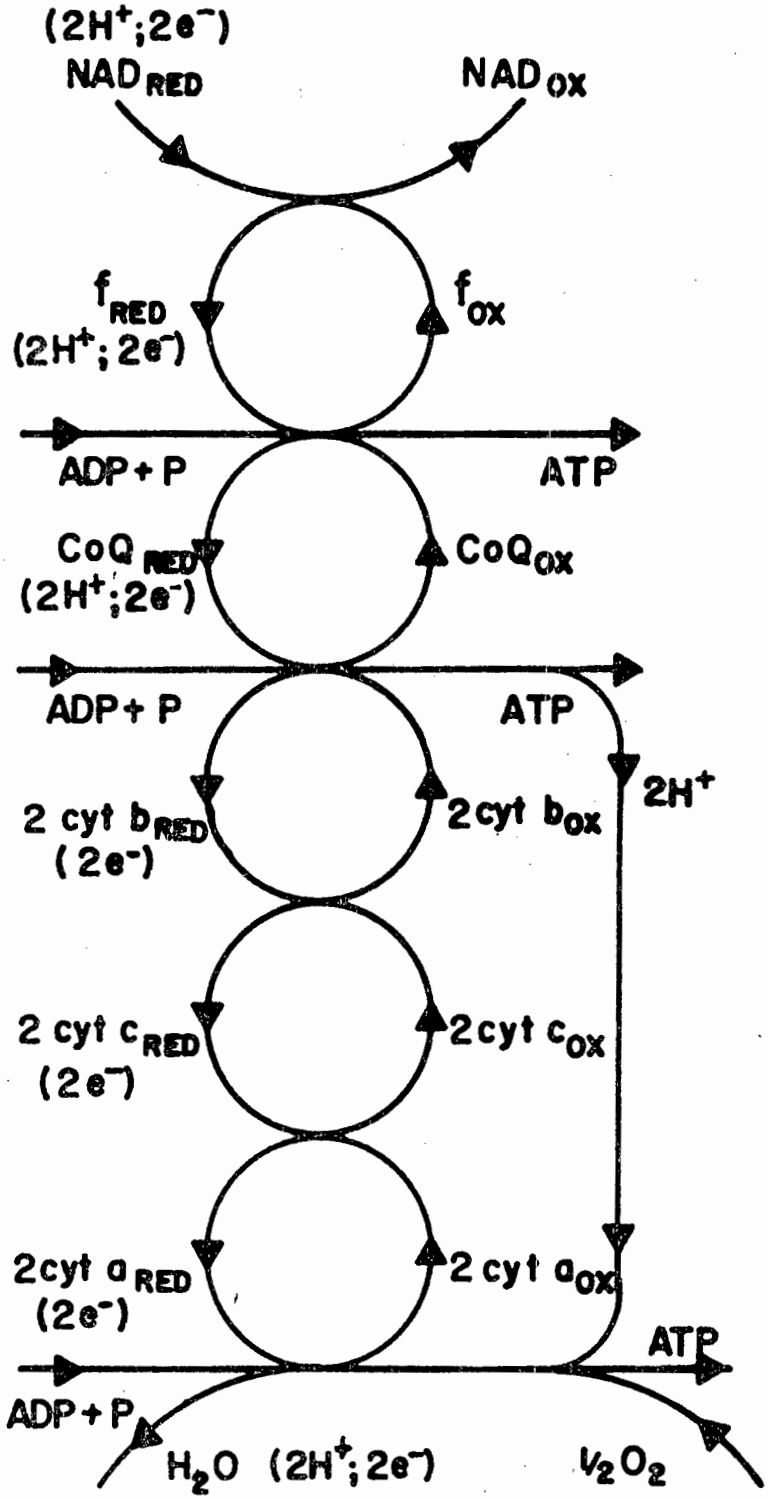

Fig 1.1a ATP (biological energy) formation by sequential oxidation-reduction reactions (e^- transport) in the cytochromes of the micro-organism.

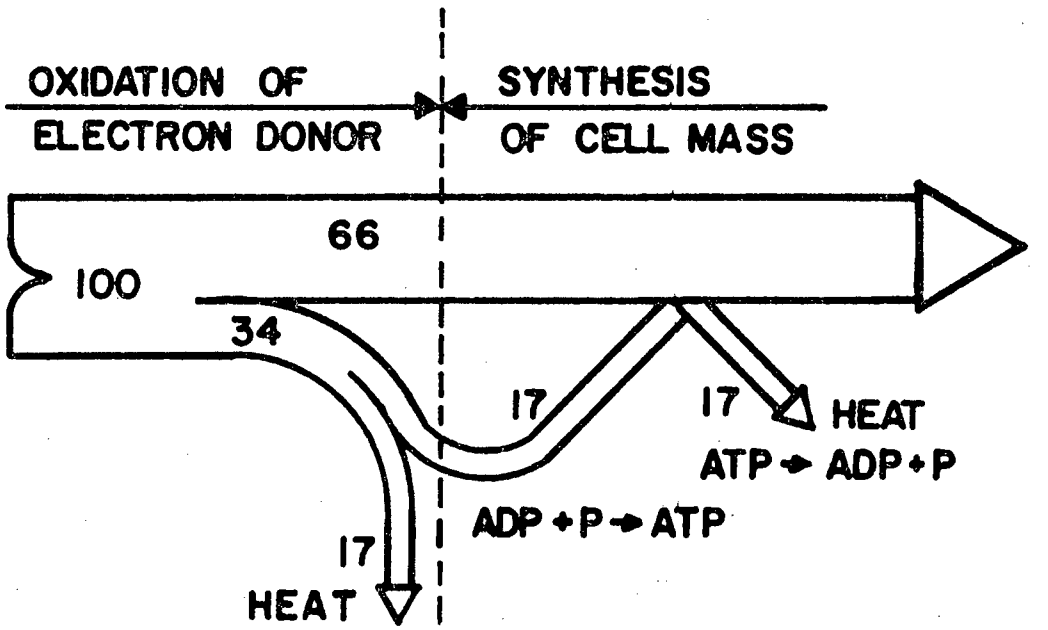

Fig 1.1b Energy change during synthesis.

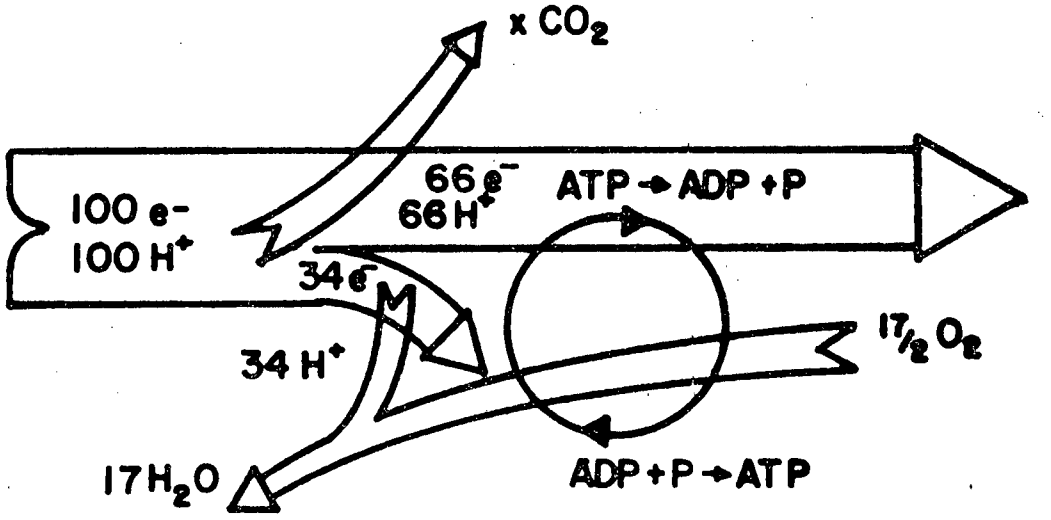

Fig 1.1c Electron changes during synthesis.

material, the free energy being lost as heat in this reorganization.

In the qualitative description above the question that arises is: "How does one quantify this synthesis reaction?" The quantification rests on the indestructability (conservation) of matter in chemical reactions. During synthesis, in the set of redox reactions, electrons and hydrogen ions are transferred from the donor to the acceptor (see Fig 1.1) but, the electrons can be neither created or destroyed; however, they can be measured, as follows: The number of electrons accepted in the reduction of a molecule of oxygen to water is a defined physical-chemical quantity. If the carbonaceous material is oxidized completely to CO_2, with oxygen as acceptor, the mass of oxygen consumed gives a direct stoichiometric measure of the electrons transferable from the organic molecules, and, as the free energy per electron (with O_2 as acceptor) is virtually constant for all carbonaceous materials, indirectly a measure of the free energy also is obtained. Thus, in a synthesis reaction, by (1) oxidizing completely the input biodegradable material and (2) oxidizing completely the synthesized material, the ratio

$$\frac{\text{oxygen demand of synthesized material}}{\text{oxygen demand of input material}}$$

$$= \frac{O_2 \text{ equivalent of synthesized material}}{O_2 \text{ equivalent of input material}}$$

$$= \frac{\text{electrons available in synthesized material}}{\text{electrons available in input material}}$$

= specific *yield* coefficient of the reaction.

Very closely the specific yield coefficient above also reflects the ratio

$$\frac{\text{free energy in the synthesized material}}{\text{free energy in the input material.}}$$

The difference between - (O_2 equivalent of input material) and (O_2 equivalent of synthesized material) - reflects the electrons

transferred to oxygen in order to release free energy to drive the synthesis reaction i.e.,

$$O_2 \text{ demand} = (O_2 \text{ equivalent of input material}) - (O_2 \text{ equivalent of synthesized material}). \quad (1.1)$$

This equation is stoichiometrically exact and forms the basis for fundamental investigations into the description of the activated sludge process. Very closely, in fact for all practical purposes exactly, it also reflects the energy changes in aerobic and anoxic redox reactions. Thus, by the developments above, we can trace the energy changes by measuring the electrons (as equivalent oxygen) in the input material and the electrons contained in the synthesized material, the difference between these two is equal to the oxygen utilized during change in state of the material. Electrons, being indestructible, can and should always be accounted for in any investigation. This brings to the fore the importance of *mass balances* to check the validity of investigations both in research and in the operation of a plant.

During nitrification ammonia serves as the electron donor and oxygen as the acceptor, to convert NH_4^+ to NO_2^- and NO_3^-. Ammonia is present in the influent either as an NH_3 radical in protein molecules (albuminoid ammonia) or as dissolved ammonia (NH_3) and ammonium ions (NH_4^+) (free and saline ammonia respectively). On conversion of the proteinaceous ammonium radical to the free and saline form (by the heterotrophs) it becomes available as an electron donor with oxygen as acceptor to form NO_3^- and NO_2^-. As the molecular forms of both NH_4^- and NO_3^- are fixed, once the total mass of nitrogen available for nitrification is known the oxygen necessary to oxidize it is also known, and hence the electron donor capacity.

One last point: The yield as defined earlier, is always an experimentally derived value. Biochemistry is now sufficiently advanced to allow the yield to be calculated theoretically fairly accurately by taking into account the stoichiometry of the electron donor and acceptor, the thermodynamic free energy released per electron transferred and the biochemical pathways through which the transfer

takes place (for example, the Embden-Meyerhof pathway - Krebs cycle sequence (Payne,1971). Such an approach, although of importance conceptionally, is not so valuable practically because in waste water treatment plants, the microbiological mass does not consist of pure culture but comprises a complex ecological system of primary organisms and ones that prey on them.

3. CARBONACEOUS ENERGY MEASUREMENT

3.1 Chemical Oxygen Demand Test

The discussion in the previous section, in which it was shown that the energy changes in biological reactions is reflected in the number of electrons transferred, led to the conclusion that the electron donor capacity can be measured in terms of the oxygen required to oxidize the carbonaceous matter to CO_2. Such a measurement is available in the Chemical Oxygen Demand (COD) test.

In the COD test the electron donor capacity of carbonaceous material is measured by oxidizing the material by a strong oxidant i.e. a hot dichromate sulphuric acid solution, in which the electro-acceptor is oxygen. This oxidant is so strong that oxidation of the carbonaceous matter is complete, or very near complete. From the half reaction for the reduction of oxygen,

$$4\,\bar{e} + 4\,H^{+} + O_2 \rightarrow H_2O$$

it can be seen that 1 mole of molecular oxygen (32g) is equivalent to 4 electron equivalents. Stoichiometrically in the COD test when the equivalent of 1g O_2 is used up then the mass of COD oxidized is also 1g, i.e.

$$1g\ COD \equiv 1g\ O_2 \equiv 1/8 \text{ electron equivalent.}$$

The COD test, therefore, supplies the information required to trace the electron and associated energy changes in a process.

Ammonia is not oxidized in the test so that the test reflects only the electron donor capacity of carbonaceous material.

In practical application some organic material is not oxidized by the COD test under any circumstances, such as the

aromatic hydrocarbons and pyridenes, although these are utilized by micro-organisms. Poor estimates of COD can also arise with lower fatty acids such as acetate because these compounds are in the unionized form at the low pH at which the test is performed - the unionized molecules can be extremely difficult to oxidize; in this regard addition of a catalyst silver sulphate overcomes the problem to a large degree to give virtually 100% oxidation.

In performing a COD test it should be remembered that the test involves a time dependent reaction and the specified refluxing period of 2 hours must be adhered to to ensure complete or near complete oxidation. Furthermore, the degree of oxidation is subject to mass action effects - equivalent masses of the same organic compound refluxed at different final test volumes yield different results for the COD; the temperature at which the refluxing step takes place also affects the oxidation rate, the refluxing temperature in turn is dependent on the concentration of sulphuric acid in the test. These factors have all been considered in the development of the COD test procedure. Hence, the COD test will give reliable results only if the test is done in strict accordance with the set procedures, for example, those in Standard Methods. If these procedures are strictly followed our experience is that the COD test adequately reflects the electron donor capacity of the sample. Application of COD test results to carbonaceous material mass balances on activated sludge plants at steady state also indicate that with careful experimental work mass balances between 98 and 102 percent are obtainable i.e. the mass of influent COD per day can be accounted for by the sum of the daily mass of oxygen utilized and the daily masses of COD in the waste sludge and effluent. Extensive investigations into COD balances by Schroeter, Dold and Marais (1983) have indicated that where poor balances are obtained, invariably the causes can be traced to errors in oxygen demand for nitrification (to correct the total oxygen demand to the carbonaceous oxygen demand) and/or errors in the oxygen utilization rate measurement.

3.2 Total Oxygen Demand (TOD) Test

In the TOD test the sample is oxidized at high temperature in a combustion oven. The TOD is the mass of oxygen required for the oxidation of all oxidizable material contained in a unit volume of wastewater sample; both carbonaceous and nitrogenous compounds are oxidized. A problem with this test is that the amount of oxygen available in the combustion oven influences the degree of oxidation of ammonia and organic nitrogen - with oxygen in excess there is a conversion of nitrogenous material to nitric oxide, whereas when oxygen is not in excess, oxidation of the nitrogenous material may be partial only. Furthermore, nitrate, nitrite and dissolved oxygen in the sample influence the TOD test result. Because the test determines both the carbonaceous and nitrogenous oxidation potential, an additional TKN test is required to isolate the carbonaceous fraction of the TOD. At the present stage of development of the test, difficulty is found in obtaining representative and reproducible readings for samples which contain particulate matter - these samples must be thoroughly homogenised to obtain representative readings as the sample volume is extremely small (10 - 20 $\mu\ell$). Sample homogenisation also increases the dissolved oxygen contamination. The difficulties of applying the TOD test to wastewater can be overcome, but the resulting test procedure reduces its attraction for general routine use.

3.3 Biochemical Oxygen Demand (BOD_5 Test)

This test provides a measure of the oxygen consumed in the biological oxidation of carbonaceous material in a sample over 5 days at 20°C. According to Gaudy (1972) the origins of this test can be traced back about a hundred years to Frankland who appears to have been amongst the first to recognise that the observed oxygen depletion in a stored sample is due to the activity of micro-organisms. The Royal Commission on Sewage Disposal appears to have developed the concept of using the oxygen depletion as a measure of the strength of pollution. Over the past century extensive research towards elucidating the meaning of the test, quantifying it and integrating it in theoretical descriptions of waste water

treatment processes, has been undertaken. To date the BOD test is still the most popular parameter for assessing the pollution strength of influents and effluents and for describing the behaviour of treatment processes. Its continued popularity seems to stem mainly from the body of experience that has built up in its use. Whereas there is justification for retaining it in effluent descriptions for regulatory purposes, in so far as present day scientific descriptions of treatment process is concerned few cogent arguments for its use over that of the COD can be produced.

The main deficiency of the BOD test arises from the inadequacy with which it assesses the electron donor capacity of the carbonaceous organic material in a sample. At the end of 5 days some of the biodegradable carbonaceous material originally present in the sample remains as unbiodegradable material. Consequently, it is not possible to perform a mass balance even with respect to the biodegradable input material. Furthermore unbiodegradable material originally present in the sample remains unaffected by the test so that there is no procedure, related to the test, whereby an assessment of this fraction can be obtained. (In contrast in the COD test, because the total electron donor capacity is measured, even though the unbiodegradable fractions are not isolated in the test, it is possible to estimate these fractions from the test results and the kinetic behavioural patterns of the treatment process).

Despite the deficiencies listed above, if the BOD_5 value constituted a *consistent* estimate it could still have provided a relative measure of practical usefulness, but even this cannot be guaranteed. Gaudy (1972) in a thought provoking review on the BOD gave a summary of the work on the BOD test (in which he took a leading part). He concluded that the standard approach to formulating the BOD time curve as a first order reaction is quite invalid: The actual curve arises from two main effects, (1) bacterial synthesis from the biodegradable input - a reaction usually complete in one to two days, and (2) predator growth using the synthesized bacteria as substrate. The second phase, being dependent on the

first, usually lags the first so that a distinct "pause" or "plateau" in the time curve is exhibited (see Fig 1.2). The occurrence and duration of this pause is dependent on the bacteria-prey relationship initially present in the sample, the "strength" of the organic material, presence of inhibitory substances and so on. These compound effects certainly are not reflected by a first order formulation. Furthermore, should nitrification occur during the 5 days the BOD value can be completely misleading; this may not be apparent unless procedures to suppress nitrification are imposed on the test. Evidently the BOD_5 value is subject to a number of influences which can be present in varying degrees resulting in unknown variable effects on the observed value.

Perhaps, the neatest summing up of the use of the BOD test is that due to Hoover, Jacewics and Porges (1953): "The BOD test is paradoxical. It is the basis of all regulatory actions and is used routinely in almost all control and research studies on sewage and industrial waste treatment. It has been the subject of a tremendous amount of research, yet no one appears to consider it

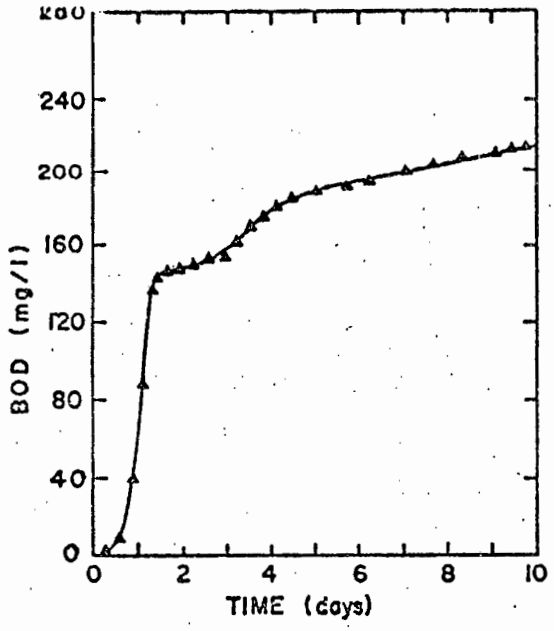

Fig 1.2 Typical experimental BOD time curve on wastewater sample with heterogeneous seed clearly showing the "pleateau" behaviour after about 1,5 days.

adequately understood or well adapted to his own work". Considered in the light of the biochemical descriptions of biological growth these remarks are still pertinent today.

3.3 Total Organic Carbon (TOC) Test

In the TOC test the sample is oxidized in a combustion chamber in the presence of oxygen and the carbon dioxide content of the burnt gasses is measured. If the organic carbon content only is required, then it is necessary to have a pre-treatment stage in sample preparation by acidification and CO_2 purging by sparging, or, to do an additional test in which the inorganic carbon only is measured. The older instruments can only measure the carbon content of soluble organic material but newer models can deal with particulate organic material.

As a procedure to estimate the electron donor capacity of the sample the TOC test can be very misleading. This arises from the fact that the ratio of organic carbon to electrons is not constant for different organic materials. For example taking glucose and glycerol:

The number of available electrons may be determined by

(i) measuring the number of moles of O_2 consumed in the complete combustion of one mole of the compound of interest, and

(ii) multiplying by four (which is the relative number of electrons required to reduce one mole of oxygen).

e.g. a) Glucose, $C_6 H_{12} O_6$

$$C_6 H_{12} O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$$

6 moles O_2 $\Rightarrow$ 6 x 4 = 24 e' compound

i.e. 24/6 = 4 e' available per unit organic C.

b) Glycerol, $C_3 H_8 O_3$

$$C_3 H_8 O_3 + 7/12\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$$

7/12 moles O_2 $\Rightarrow \frac{7}{2}$ x 4 = 14 e' compound

i.e. 14/3 = 4,66 e' available per unit organic C.

Comparing glucose and glycerol the electron donor per unit C differs by 17%.

The analysis above points to the inadvisability of utilizing the TOC test to describe the energy based behaviour of water treatment processes. This does not mean that the test does not have other uses; it serves a valuable function as control parameter or as a parameter in tertiary treatment where the carbon content in the effluent may be of great importance.

4. COD/VSS RATIO

Consider a completely biodegradable soluble substrate, for example glucose. If a sample of glucose solution is innoculated with bacteria, syntheses of new bacterial mass will occur. The change in soluble COD, ΔCOD(soluble), will be reflected in an increase in the COD of the bacterial mass, ΔCOD(bacteria), and oxygen utilized to generate free energy, ΔO_2(utilized),

$$\Delta\text{COD(soluble)} = \Delta\text{COD(bacteria)} + \Delta O_2\text{(utilized)} \qquad (1.2)$$

Equation (1.2) reflects the destination of the electrons from the donor to the synthesized material and the electron acceptor oxygen. From extensive work reported in bacteriology, reviewed by Payne (1971), the fraction of ΔCOD(soluble) appearing as ΔCOD(bacteria) appears to be nearly constant. Usually the fraction is expressed as a ratio called the specific yield coefficient Y_{COD} (see Eq 1.1) i.e.

$$\Delta\text{COD(bacteria)}/\Delta\text{COD(soluble)} = Y_{COD} \qquad (1.3)$$

Equation 1.2 can be rewritten in terms of Y_{COD}

$$\Delta\text{COD(soluble)} = Y_{COD}.\Delta\text{COD(soluble)} + \Delta O_2 \qquad (1.4)$$

and recasting Eq (1.4)

$$\Delta O_2 = (1 - Y_{COD})\ \Delta\text{COD(soluble)} \qquad (1.5)$$

In wastewater treatment kinetics the usage has arisen, probably from

the work of bacteriologists, to measure the mass of *volatile solids generated* in the synthesis reaction, X_a, rather than the COD of the volatile solids generated, ΔCOD(bacteria). To retain the usefulness of Eq (1.4), in particular in the form given by Eq (1.5), it is necessary to relate ΔX_a to ΔCOD(bacteria). The usage has developed to express the relationship between ΔX_a and ΔCOD(bacteria) by the ratio of the two parameters, called the COD/VSS ratio, defined by the symbol f_{cv},

$$f_{cv} = \text{COD/VSS} = \Delta\text{COD(bacteria)}/\Delta X_a$$

Using this definition the yield coefficient Y_{COD} is expressed in terms of a specific yield coefficient with respect to volatile solids Y_h, and the COD/VSS ratio, f_{cv},

$$Y_{COD} = f_{cv} \cdot Y_h \qquad (1.6)$$

and inserting in Eq (1.5),

$$\Delta O_2 = (1-f_{cv}Y_h)\ \text{COD(soluble)} \qquad (1.7)$$

Equation (1.7) is very important in biological wastewater treatment kinetics.

Considerable research has been undertaken to establish a value for f_{cv} and to determine the factors effecting it. Theoretically f_{cv} has been evaluated by accepting an empirical stoichiometric formulation for biological sludge, for example that by Hoover and Porges (1952),

$$C_5H_7O_2N + 5O_2 \rightarrow 5CO_2 + 2H_2O + NH_3$$

Stoichiometrically,

113g VSS → 160gm O → 160gm COD

i.e. 1gm VSS → 1,42mg COD

i.e. COD/VSS = 1,42mg COD/mg VSS

Eckenfelder and Weston (1956) presented experimental data that supports this theoretical ratio. However other theoretical ratios

have been proposed and each find some experimental confirmation, see Table 1.1. The basic difficulty in evaluation of f_{cv} arises from the fact that f_{cv} is a ratio so that the small random errors in either the COD or the VSS magnify the dispersion of the ratio; a reasonably stable mean estimate of the f_{cv} value of a sludge requires at least thirty COD and VSS pair determinations. With smaller numbers the mean f_{cv} value can still vary significantly.

Considering the COD/VSS ratio of sludges derived from activated sludge processes treating municipal effluents, it should be remembered that not only is active volatile mass generated but volatile mass is also present in unbiodegradable particulate form in the influent (and accumulates in the sludge mass) and inert biological residue is generated due to endogenous respiration (and also accumulates in the sludge mass). Consequently the sludge normally consists of three fractions, active, inert influent and endogenous. Each of these could have a different f_{cv} value, a factor not considered in deriving the theoretical ratios discussed earlier. The proportions of the three fractions in a sludge depend on the sludge age, the active fraction being relatively small at long sludge ages and high at short sludge ages. For practical purposes an important aspect, therefore, is whether f_{cv} changes with sludge age or whether a mean experimentally derived value can be assigned to all activated sludges. Accordingly Marais and Ekama reported on COD/VSS ratio of activated sludge from laboratory scale units treating municipal wastewater for sludge ages ranging from 2 to 30 days. Their data indicate that despite the significant changes in proportion of the three fractions with changes in sludge age, f_{cv} appeared to remain substantially constant, at 1,48 mgCOD/mgVSS. This finding is very important because it allows that COD balances generally can be performed using VSS measurements on the waste sludge.

Table 1.1 Theoretical COD values for various empirical formulations for microbial sludge (after McCarty, 1964).

Bacterial Formulation	Molecular Weight	Theoretical COD in Grams			
		Per Mole	Per gm TSS	Per grm VSS	Per gm Carbon
$C_5H_7O_2N$	113	160	1,28	1,42	2,67
$C_5H_9O_3N$	131	160	1,10	1,22	2,67
$C_7H_{10}O_3N$	156	232	1,33	1,48	2,76
$C_5H_8O_2N$	114	168	1,32	1,47	2,80

5. REFERENCES

1. Eckenfelder W W and R F Weston (1956) Kinetics of Biological Oxodation. In Biological Treatment of Sewage and Industrial Wastes Vol 1. Eds.B J McCabe and W W Eckenfelder, Rheinhold Publ.Co. New York, 18-34.

2. Gaudy A F (1972) Water Pollution Microbiology. Ed.R Mitchell, Wiley Interscience, New York.

3. Hoover S R, L Jasewicz and N Porges (1953) An Interpretation of the B.O.D Test in terms of Endogenous Respiration of Bacteria. Sewage and Industrial Wastes, 25, 1163-1173.

4. Marais G v R and G A Ekama (1976) The Activated Sludge Process Part 1 - Steady State Behaviour, Water SA, 2, 164-200.

5. McCarty P L (1964) Thermodynamics of Biological Synthesis and Growth, 2nd Int. Conf. Wat. Poll. Research, Pergamon Press, New York, 169-199.

6. Payne W J (1971) Energy yields and growth of heterotrophs. Annual Review, Microbiology, 17-52.

7. Phelps E B (1944) Stream Sanitation, John Wiley Inc., New York.

8. Schroeter W D, P L Dold and G v R Marais (1982) The COD/VSS Ratio of the Volatile Solids in the Activated Sludge Process, Res.Rept No W 45, Dept. of Civil Eng., Univ. of Cape Town.

CHAPTER TWO

NATURE OF MUNICIPAL WASTEWATERS

G 'A Ekama and G v R Marais

1. WASTEWATER CHARACTERIZATION

In so far as it affects biological treatment, municipal waste flows can be characterized chemically and physically.

Chemical characterization comprises identification and measurement of: (a) Carbonaceous and nitrogenous constituents in their various fractions, soluble and particulate, biodegradable and unbiodegradable, and (b) Inorganic constituents principally total alkalinity (Alkalinity) total acidity, pH and phosphorus. Inorganic constituents such as calcium, sodium, magnesium, chloride and sulphate usually are of minor importance with the exception of calcium which, in certain circumstances, can be of significance in phosphorus removal by calcium-phosphate precipitation.

Physical characterization comprises separation of the wastewater into dissolved, suspended and settleable constituents.

2. CHEMICAL CHARACTERIZATION

2.1 Carbonaceous materials

Characterization of the carbonaceous material in the influent is done via the Chemical Oxygen Demand (COD) test. For activated sludge process design it is necessary to identify and know the magnitudes of the various fractions of the influent COD as these significantly affect the response of the process. Research at the University of Cape Town has indicated that the subdivisions shown diagrammatically in Fig 2.1 are essential for accurate description of the behaviour of the process.

2.1.1 Biodegradable and unbiodegradable fractions

From Fig 2.1 the first major subdivision is into biodegradable COD (S_{bi}) and unbiodegradable COD (S_{ui}) fractions. This division is important for the following reasons: In design, knowing biodegradable COD concentration and the flow per day gives the biodegradable COD load on the plant; knowing the mass of

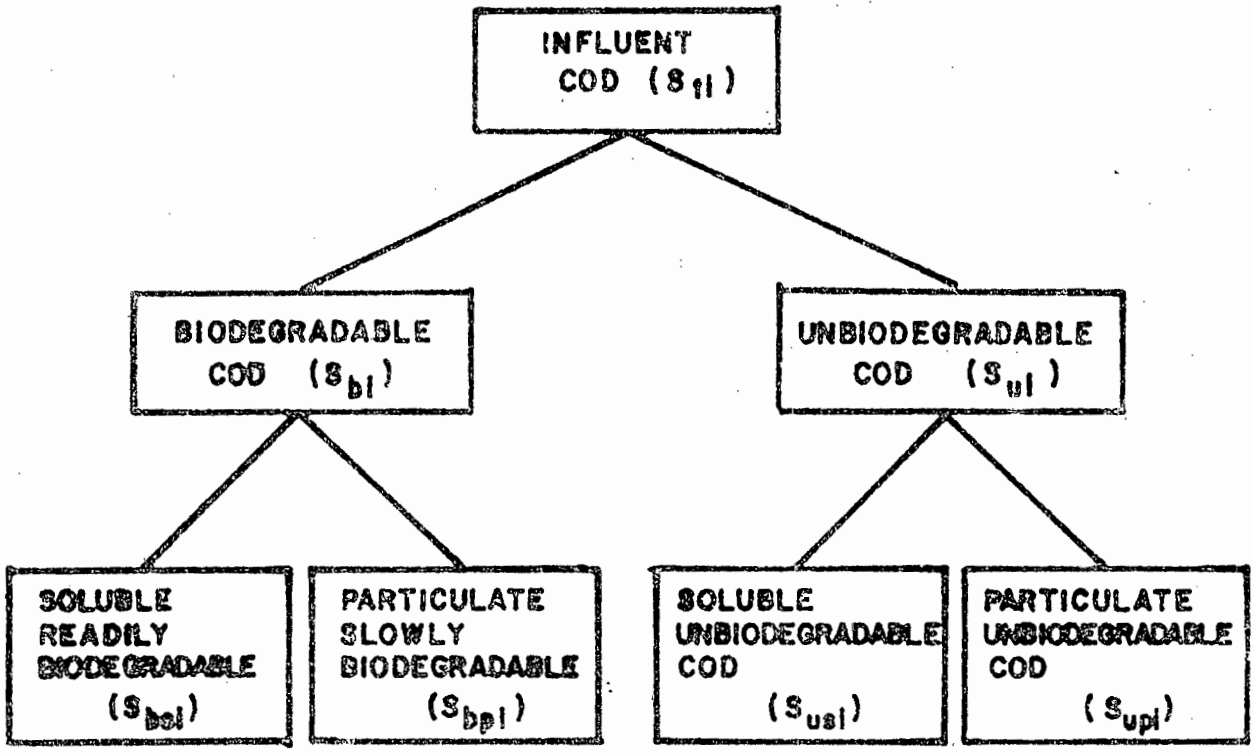

Fig 2.1 *Division of the total influent COD in municipal wastewaters into its various constituent fractions*

the total COD concentration S_{ti}, i.e.

$$S_{usi} = f_{us} S_{ti} \quad (2.3)$$

$$S_{upi} = f_{up} S_{ti} \quad (2.4)$$

where

f_{us} = unbiodegradable soluble COD fraction with regard to the total COD (mgCOD/mgCOD)

f_{up} = unbiodegradable particulate COD fraction with regard to the total COD (mgCOD/mgCOD).

Hence from Eq (2.2)

$$S_{ui} = (f_{us} + f_{up}) S_{ti} \quad (2.5)$$

The particulate unbiodegradable COD concentration may be expressed also in terms of volatile solids, X_{ii}:

$$X_{ii} = S_{upi}/f_{cv}$$

$$= f_{up}.S_{ti}/f_{cv} \quad (2.6)$$

where

X_{ii} = unbiodegradable particulate volatile solids concentration in the influent (mgVSS/ℓ)

f_{cv} = COD to VSS ratio of the solids

= 1,48 mgCOD/mgVSS.

Biodegradable COD fractions:

The biodegradable COD concentration is found from Eq (2.1) as follows:

$$S_{bi} = S_{ti} - S_{ui}$$

and from Eq (2.5)

$$= S_{ti} - S_{ti} (f_{up} + f_{us})$$

$$= S_{ti} (1 - f_{up} - f_{us}) \qquad (2.7)$$

From Fig 2.1 the *biodegradable* COD, S_{bi}, is divided into *readily biodegradable soluble* COD, S_{bsi}, and *slowly biodegradable particulate* COD, S_{bpi}. Each can be expressed in terms of S_{bi} as follows:

$$S_{bsi} = f_{bs} S_{bi} \quad \text{and} \qquad (2.8a)$$

$$S_{bpi} = (1 - f_{bs}) S_{bi} \qquad (2.9a)$$

where

f_{bs} = readily biodegradable COD fraction with respect to the *biodegradable* COD.

The readily biodegradable COD can also be expressed in terms of the *total* COD, S_{ti}, i.e. substituting for S_{bi} from Eq (2.7) in Eq (2.8) yields

$$S_{bsi} = f_{bs} (1 - f_{up} - f_{us}) S_{ti} \qquad (2.8b)$$

$$= f_{ts} S_{ti} \qquad (2.9b)$$

where

f_{ts} = readily biodegradable COD fraction with respect to the total COD.

2.2 Nitrogenous materials

Characterization of the nitrogenous material in the influent is with the Total Kjeldahl Nitrogen (TKN) and free and saline ammonia tests. As for the carbonaceous material, the nitrogenous material also is subdivided into different fractions but in a different fashion from that for the carbonaceous material. The subdivision is shown in Fig 2.2.

In certain wastewaters nitrate and nitrite might be present; the TKN test does not include these. The vast majority of municipal effluents will not contain nitrate or nitrite because in most sewerage systems the wastewater will be in an unoxygenated state and any nitrate entering the system is likely to be denitrified before it reaches the wastewater treatment plant.

2.2.1 Free and saline and proteinaceous fractions

The free and saline ammonia fraction, N_{ai}, is determined by a test of this name. The preteinaceous or organic fraction is determined by difference between the TKN, N_{ti}, and free and saline ammonia values, N_{ai}.

The free and saline ammonia is immediately available for incorporation into the bacterial protoplasm and for conversion to nitrite or nitrate, if the process is appropriately designed.

The proteinaceous fraction, from Fig 2.2, consists of a number of sub-fractions, *unbiodegradable soluble* and *unbiodegradable particulate organic nitrogen* fractions, N_{ui} and N_{pi} respectively, and a *biodegradable organic nitrogen* fraction, N_{oi}. The unbiodegradable soluble fraction passes unaffected through the system and is discharged in the effluent similar to the soluble unbiodegradable COD. The unbiodegradable particulate organic nitrogen by implication must be part of the unbiodegradable particulate COD (as X_{ii}), and is treated as such, hence, this fraction leaves the process via the sludge wasted daily. The biodegradable organic nitrogen is broken down by the heterotrophs to free and saline ammonia which with its influent counterpart participates in any further biologically mediated reactions. The breakdown occurs very readily and normally it can be

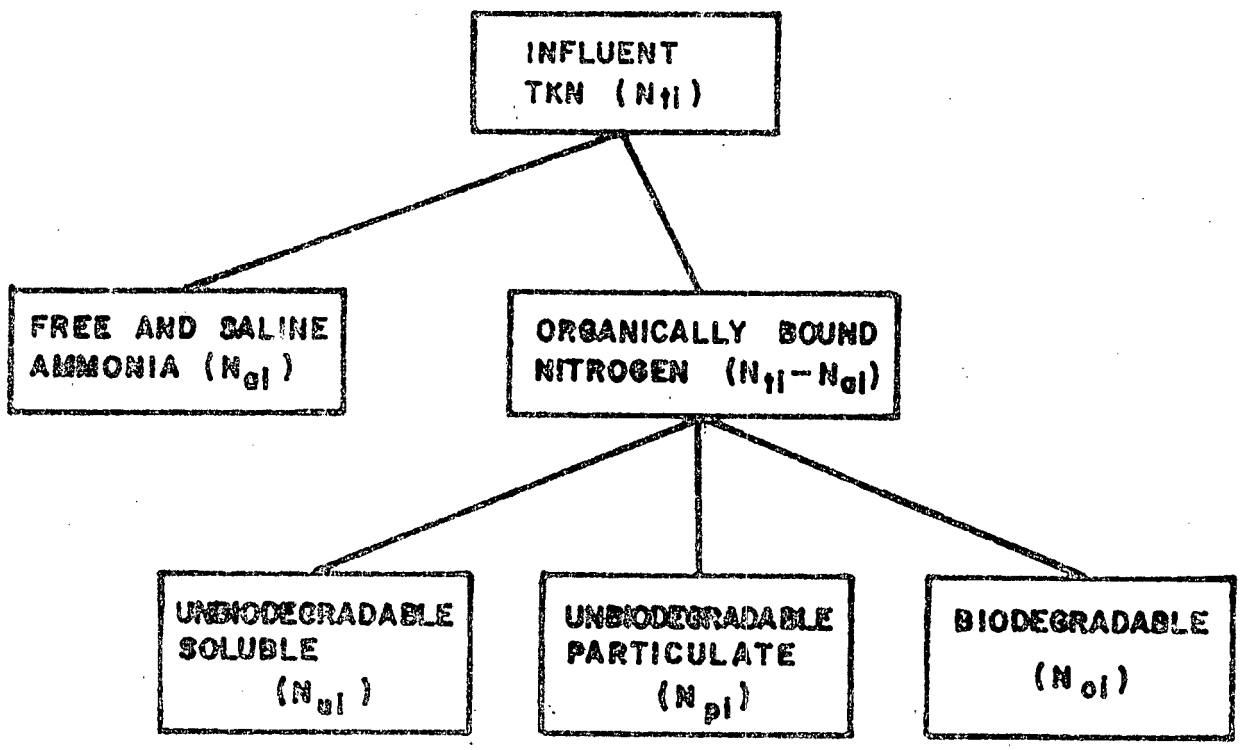

Fig 2.2 *Division of the total influent TKN in municipal wastewater into its various constituent fractions*

expected to be virtually complete for all sludge ages greater than about 3 days.

With regard to measurement of these fractions, the free and saline ammonia (N_{ai}) is measured directly by the test bearing this name; the total organic nitrogen is found from the difference between the TKN and free and saline ammonia test concentrations. Difficulties in quantification arise when subdividing the total organic nitrogen into its biodegradable and unbiodegradable fractions, N_{oi}, N_{ui} and N_{pi}, (see Fig 2.2). N_{ui} and N_{pi} are postulated by association to their counterparts in the COD subdivision. Estimates of their magnitudes can be obtained only by comparing the observed response of laboratory scale processes with that predicted by the theoretical model incorporating these fractions. From a large number of such comparisons on processes operated within the range of sludge ages from 2 to 30 days, under cyclic and steady states in the temperature range 12 to 25°C, it would appear that N_{ui} and N_{pi} are necessary in the model to obtain good and consistent correlation between observation and prediction. However, the fractions are small and it is not necessary therefore to have accurate estimates. Concurrently N_{pi} is expressed in terms of the unbiodegradable particulate volatile solids in the influent (X_{ii}) i.e. N_{pi} is 10% of X_{ii} (see Eq 2.13): from experimental data on the TKN/VSS ratio of the MLVSS in the biological reactor, using the same influent wastewater source it was found that the TKN/VSS ratio remained the same irrespective of sludge age from 3 to 30 days despite the fact that the various VSS fractions change with sludge age. Hence it is reasonable to accept that the TKN/VSS ratio of the inert organic solids is equal to that of the other VSS fractions at 0,10 mgN/mgVSS. Furthermore the unbiodegradable soluble organic nitrogen concentration (N_{ui}) apparently is very low, between 0 and 5% of the influent TKN for raw wastewaters. Later it will be shown (Chapter 5) that the N_{ui} concentration plays a very minor role in design. The suggested fractional values are listed in Table 2.1.

2.2.2 Analytical formulation

The total TKN, S_{ti} is divided into its constituents as

follows, (see Fig 2.2):

$$N_{ti} = N_{ai} + N_{ui} + N_{pi} + N_{oi} \tag{2.10}$$

where

N_{ti} = total influent TKN (mgN/ℓ)

N_{ai} = influent ammonia (mgN/ℓ)

N_{ui} = soluble unbiodegradable organic nitrogen in the influent (mgN/ℓ)

N_{pi} = particulate unbiodegradable organic nitrogen in the influent (mgN/ℓ)

N_{oi} = biodegradable organic nitrogen in the influent (mgN/ℓ)

It is convenient to express some of the fractions of nitrogen in terms of the total TKN concentrations

$$N_{ai} = f_{na} N_{ti} \tag{2.11}$$

$$N_{ui} = f_{nu} N_{ti} \tag{2.12}$$

where

f_{na} = ammonia fraction of the influent TKN (mgN/mgN)

f_{nu} = unbiodegradable soluble organic nitrogen fraction (mgN/mgN)

The unbiodegradable organic nitrogen in the particulate material, N_{pi}, is best expressed in terms of the unbiodegradable influent

volatile material, X_{ii}, or in terms of its COD counterpart, i.e.

$$N_{pi} = f_n S_{upi}/f_{cv} = f_n X_{ii} \quad (2.13)$$

where

f_n = nitrogen fraction of the influent biodegradable volatile particulate material $\cong$ 0,10 mgN/mgX_{ii}

From Eqs (2.10 to 2.13), the biodegradable organic nitrogen (N_{oi}) can be found by subtracting N_{ui}, N_{ai} and N_{pi} from N_{ti}

$$N_{oi} = N_{ti} (1 - f_{na} - f_{nu}) - f_n f_{up} S_{ti}/f_{cv} \quad (2.14)$$

The significance of the various influent TKN fractions on the design of nutrient removal activated sludge processes is discussed in Chapter 3, Section 8 and in Chapter 5, Section 3.

2.2.3 Specific growth rate of nitrifiers

Experimental observations on the number of different municipal wastewater flows have indicated that the maximum specific growth rate constant of the nitrifiers, μ_{nm}, can differ greatly in value and appears to be specific to each waste flow. The magnitude of μ_{nm} can have a significant influence on the design of nutrient removal processes, see Chapters 3, 4, 5 and 6. Therefore, for optimal design it is most desirable to have an estimate of μ_{nm}. This estimate is obtained by running a completely mixed single reactor at a sludge age of about 8 days, at 20°C imposing a sequence of aerobic and anoxic periods on it and measuring the rate of nitrate increase (or the rate of Alkalinity decrease) during the aerobic period. The data thus obtained can be analysed manually to give the μ_{nm} at 20°C, i.e. μ_{nm20}. By applying the well established relationship between μ_{nm} and temperature the value at any temperature can be determined. Details of the test procedure and analysis of the data are given in Appendix A4.

2.3 Phosphorus

The total phosphorus concentration in municipal wastewaters consists mainly of two fractions, a soluble orthophosphate (PO_4^{3-}) fraction and an organically bound phosphorus fraction which may be soluble or particulate in form. In both settled and raw municipal wastewaters, the orthophosphate fraction predominates, ranging between 70 to 90 percent of the total phosphorus.

The orthophosphate concentration* can be measured by a colorimetric test of that name. However, this measure records only the orthophosphate concentration of the influent, which may underestimate the total phosphorus in the influent by about 10 to 20 percent or more. The organically bound phosphorus is converted to orthophosphate in the activated sludge process so that the orthophosphate concentration in the influent underestimates the phosphorus to be removed in the process. For example, if the orthophosphate concentration is 8 mgP/ℓ and the total-P is 10 mgP/ℓ then for an effluent standard of 1 mgP/ℓ orthophosphate, if the plant is designed to remove 7 mgP/ℓ on the basis of the ortho-P influent concentration, the effluent actually will contain 3 mgP/ℓ ortho-P. The process should be designed to remove 9 mgP/ℓ on the basis of the total-P influent concentration. Consequently, for the influent the only reliable test is the total-P test. For the effluent, the filtered ortho-P concentration very closely approximates the filtered total-P concentration and this ortho-P test would appear to be adequate. However, in performing the ortho-P test, a problem sometimes is encountered in that the natural colour in some wastewaters interferes with the colorimetric test giving rise to spurious results.**

3. PHYSICAL CHARACTERIZATION

Physical characterization of the influent exists mainly in estimating the expected performance of the primary settling tank.

* All phosphorus and phosphate concentrations are measured relative to the phosphorus atom i.e. mgP/ℓ.

** This is a problem encountered in treated effluents from the Western Cape, but apparently is absent from treated effluents of Johannesburg and Pretoria.

The function of the settling tank is to separate in some degree the settleable particulate material from the influent flow to give a supernatant overflow having reduced values of COD, TKN and Phosphorus.

Physical characterization basically is made on the relative size of the particles in the wasteflow. Here three broad divisions are recognized, *dissolved*, *colloidal* and *suspended solids*, see Fig 2.3. Generally material of particle size smaller than 10^{-3} to 1 micron are taken as colloidal and material with particle size larger than 1 micron as suspended. To obtain estimates of the suspended material pore size membrane filters other than 1 micron are in use which can lead to significantly different results so that when reporting or interpreting data, careful note should be made of the pore size of the filter membranes (and papers) on which the data is based.

The fraction of *suspended* solids (i.e. retained on a 1 micron filter) that can be removed by gravity settling is called the *settleable* solids and usually ranges in equivalent pore size from 10 to 50 micron depending on particle density. However a more practical procedure, to estimate the mass of settleable solids in a sample of wastewater, is to use the Imhoff cone: A one litre Imhoff cone is filled with a sample and allowed to settle for two hours. The volume of solid material settled into the bottom of the cone gives a measure (in ml/ℓ) of the quantity of material that can be removed by gravity sedimentation. From a large number of tests it has been found that 1 ml/ℓ of settleable solids is approximately equivalent to a dry mass* of 25 mg/ℓ; with this equivalence it is possible to obtain an estimate of the mass of settleable solids using the Imhoff test.

The settleable solids can be measured either as *total solids* where total solids include both the organic and inorganic fractions, or, as *volatile or organic solids* where the volatile solid is the difference between the total solids and the ash remaining after the

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*mass retained on filter paper (Whatmans No.1) after drying for 12 hours at 105°C. Measurements taken from raw wastewater at the Vienna main treatment works by Von der Emde and Ekama *et al.*

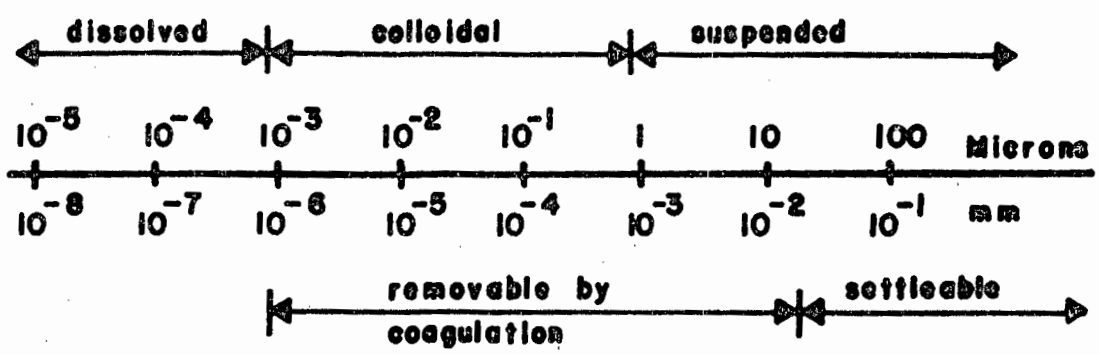

Fig 2.3 *Particle size range and classification.*

total solids are incinerated in an oven at 600°C for half an hour. At this temperature most inorganic (mineral) salts, except magnesium carbonate, do not decompose or volatilize. The ratio Volatile Solids:Total Solids of the settleable solids from municipal wasteflows is about 0,75 i.e. 75% volatile, 25% mineral so that Volatile Solids ≅ 0,75 Total Solids. The COD associated with the volatile solids can be estimated by multiplying the volatile solid mass by 1,48 i.e. COD ≅ 1,48 Volatile Solids.

The Imhoff cone test serves a means whereby the percentage removal of Total Phosphorus and TKN in the primary settling tank can be estimated. This is done by determining total-P and TKN concentrations in the waste sample before settling and in the supernatant after settling in the cone.

In a primary settling tank the degree of COD and settleable solids removed by gravity sedimentation depends on the upflow velocity (overflow rate) and retention tiem. For relatively deep tanks (>3m) with mean retention times of 2 to 3 h and mean overflow rates of 1,5 to 2 m/ℓ between 50 and 80% of the settleable solids (as given by the Imhoff cone test) and 30 to 50% (mean of 40%) of the total COD will be removed. Increasing the retention time above 3 h does not improve the removals significantly. However,lowering the retention time to say one hour (equivalent to 3 m/h mean overflow rate) reduces the removal to about half of that at 3 h retention time.

With regard to the TKN and P removal in primary tanks this can vary depending on state of the waste flow. It seems that in fresh wastewater a larger fraction of the TKN and P may be bound to the settleable solids than if the wastewater is old and solubilization of the TKN and total P fractions has occurred. Unfortunately insufficient information on these aspects is available to lay down criteria for design. For design it would seem preferable to assume that solubilization does occur so that only a minor fraction of the TKN and P respectively is removed by primary sedimentation, between 15 and 25%, even though there are reported removals of up to 40%.

The discussion above indicates that with primary sedimentation

a significant reduction is obtained in COD (40%) but a smaller reduction of TKN and total P (15 to 20%). This has the effect that settled wastewater has increased TKN/COD and P/COD ratios compared to the raw wastewaters. Note also that the readily biodegradable COD concentration (S_{bsi}) which is completely in the dissolved form is not reduced so that the concentrations in the raw and settled flow are the same, hence the fraction S_{bsi}/S_{ti} increases for settled sewage. With regard to the unbiodegradable particulate COD this fraction appears to be largely removed by primary sedimentation so that settled wastewaters contain low fractions of unbiodegradable particulate COD.

4. QUANTIFICATION OF WASTEWATER CHARACTERISTICS

In the above section the various chemical and physical wastewater characteristics were defined. In this section these characteristics are quantified to facilitate their use in design. The influence of the various characteristics on the design of an activated sludge process is discussed in Chapter 3.

The ranges of the magnitudes of the various chemical and physical characteristics of approximately normal *raw* and *settled* municipal wastewaters are listed in Table 2.1. The variability of municipal wastewaters is such that it is difficult to give smaller ranges for these characteristics. Generally it has been found that the greater the diversity and larger the community from which the wastewater originates, the less the characteristics will vary during the life of the plant. Also the greater the diversity and larger the community, the smaller the daily variations in wastewater characteristics and flow.

A diagrammatic representation of the magnitudes of the different COD and TKN fractions in an approximately normal *raw* municipal wastewater is shown in Figs 2.4 and 2.5 respectively. With regard to the COD fractions, Fig 2.4 shows that about 7% of the total COD is soluble unbiodegradable, 13% particulate unbiodegradable, 60% particulate slowly biodegradable and 20% soluble readily biodegradable. With regard to the TKN fractions, Fig 2.5 shows that about 3% of the total TKN is soluble unbiodegradable organic nitrogen, 10% particulate unbiodegradable organic nitrogen associated with the particulate

Table 2.1 Approximate average municipal wastewater characteristics for raw and settled wastewaters in South Africa.

Wastewater Characteristic	Raw	Settled
1. Influent COD (mgCOD/ℓ)	500-800	300-600
2. Influent BOD_5 (mgBOD/ℓ)	250-400	150-300
3. Influent TKN (mgN/ℓ)	35-80	30-70
4. Influent Phosphorus (mgP/ℓ)	8-18	6-15
5. Total Suspended Solids (mg/ℓ)	270-450	150-300
6. Settleable Solids in (mg/ℓ)	150-350	0-50
in (ml/ℓ)**	6-14	0-2
7. Non-Settleable Solids (mg/ℓ)	100-300	100-300
8. TKN/COD ratio (mgN/mgCOD)	0,07-0,10	0,09-0,12*
9. Total P/COD ratio (mgP/mgCOD)	0,015-0,025	0,020-0,030*
10. Unbio.particulate COD fraction (f_{up})	0,07-0,20	0,00-0,10
11. COD/VSS ratio of unbio.particulate COD (f_{cv}) (mgCOD/mgVSS)	1,45-1,50 ave.1,48	1,45-1,50 ave.1,48
12. TKN/VSS ratio of unbio.particulate COD (f_n) (mgN/mgVSS)	0,09-0,12 ave.0,10	0,09-0,12 ave.0,10
13. Unbio.soluble COD fraction (f_{us})	0,40-0,10	0,05-0,20*
14. Fraction Biodegradable COD (S_{bi}/S_{ti})	0,75-0,85	0,80-0,95
15. Readily Biodegradable COD with respect to total (f_{ts})	0,08-0,25	0,10-0,35*
16. Maximum specific growth rate of the nitrifiers (/d)	0,20-0,70	0,20-0,70
17. Ammonia/TKN fraction (f_{na})	0,60-0,80	0,70-0,90*
18. Unbio.soluble TKN fraction (f_{nu})	0,00-0,04	0,00-0,05*
19. Minimum Temperature (°C)	10-15	10-15
20. Maximum Temperature (°C)	20-30	20-30
21. Alkalinity (mg/ℓ as $CaCO_3$)	200-300	200-300

*Note that the characteristics of settled wastewater should be selected in conformity with the characteristics of the original raw wastewater and primary settling tank behaviour (see Chapter 4, Section 12.1).

** Volume settled in a 1ℓ Imhoff cone in 2 hours.

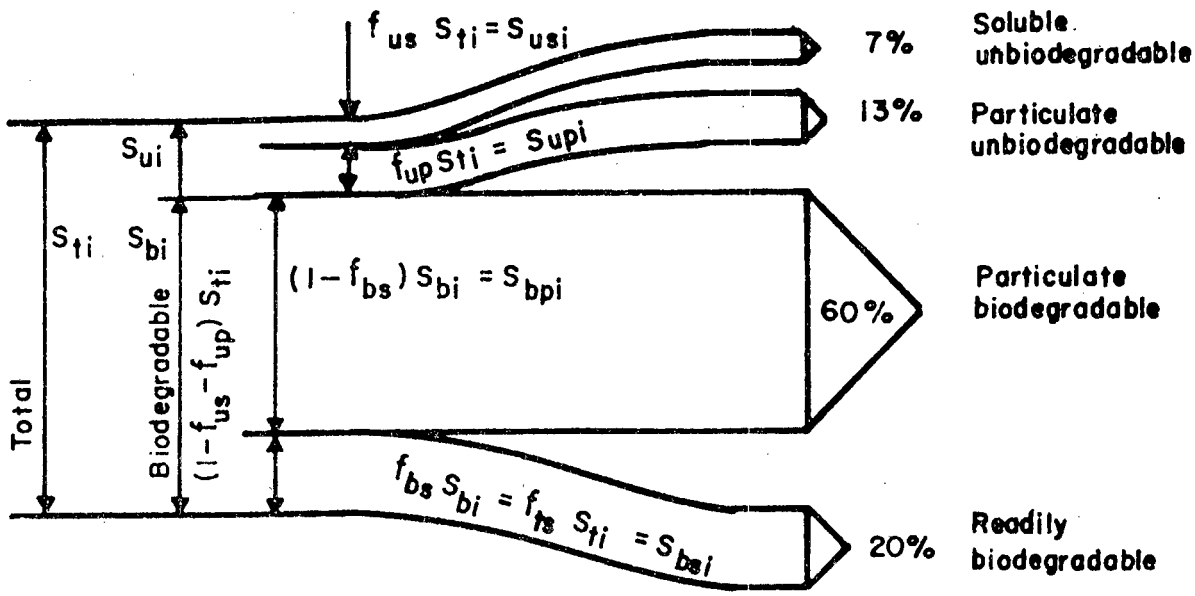

Fig 2.4 *Diagrammatic representation of the different fractions of the total influent COD concentration. Numerical values apply to raw municipal wastewater.*

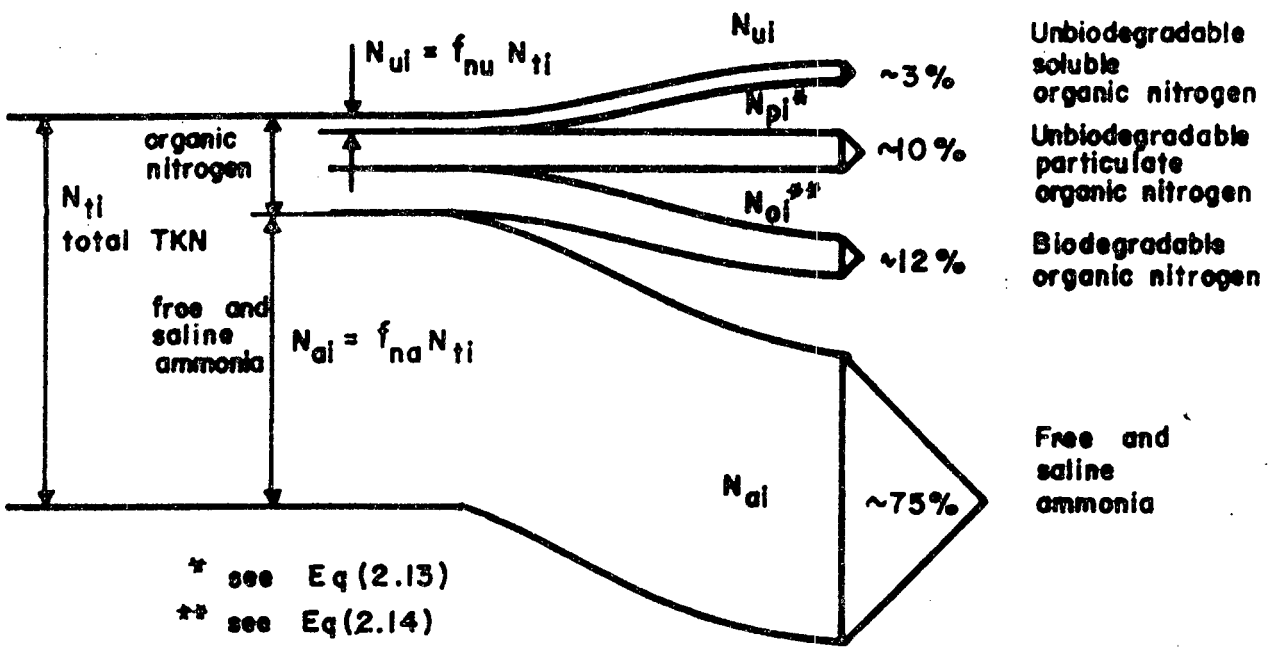

Fig 2.5 *Diagrammatic representation of the various fractions of the influent TKN in municipal wastewater. Numerical values apply to raw municipal wastewater.*

unbiodegradable COD, 12% biodegradable organic nitrogen and 75% free and saline ammonia.

Caution should be exercised when selecting an f_{up} value: social organization of the community for whom the wastewater treatment process is envisaged must be critically examined. For example, analysis of data reported by Sutton *et al.* (1979) from Canada, indicates that the f_{up} fraction is 0,25 for raw wastewater. It appears that the use of garbage grinders in Canada significantly increases the f_{up} fraction. This demonstrates the pitfalls in selecting wastewater characteristics uncritically and without due recognition of the factors which contribute to the nature and composition of the wastewater. It also demonstrates the dangers of applying uncritically technology developed overseas to local conditions and *vice versa*.

5. REFERENCES

1. Dold P L, G A Ekama and G v R Marais (1980) A general model for the activated sludge process, Prog.Wat.Tech., 12, Tor 47-77.

2. Marais G v R and G A Ekama (1976) The activated sludge process part I - steady state behaviour, Water SA, 2, 4, 163-200.

3. Levenspiel O (1972) Chemical Reaction Engineering 2nd Ed., John Wiley, New York, 465-469.

4. Sutton P M, B E Jank, B A Monaghan and K L Murphy (1979) Single sludge nitrogen removal systems. Research Report No 88, Water Technology Centre, Burlington, Canada.

CHAPTER THREE

INFLUENCE OF WASTEWATER CHARACTERISTICS ON PROCESS DESIGN

by

G A Ekama and G v R Marais

1. INTRODUCTION

In this chapter considerations in the design of nutrient removal activated sludge processes are qualitatively described to provide a background for the subsequent chapters in which the process design for COD removal only (Chapter 4), nitrification (Chapter 5), nitrification-denitrification (Chapter 6) and biological phosphorus removal (Chapter 7) are quantitatively set out - in these chapters, detailed equations, design charts, sample calculations and recommendations for design are presented.

2. RELATIVE IMPORTANCE OF CHARACTERISTICS

In the design of activated sludge processes the characteristics of the wastewater are of prime importance. These characteristics govern both the selection of the process and the removals of nitrogen and phosphorus attainable in the process.

Influent wastewater characteristics of crucial importance are:

(1) Mean influent COD and TKN concentrations (S_{ti} and N_{ti} respectively) and mean daily flow (Q)

(2) Influent readily biodegradable COD fraction (f_{bs})

(3) Influent TKN/COD concentration ratio (N_{ti}/S_{ti})

(4) Influent (Total P)/COD concentration ratio (P_{ti}/S_{ti})

(5) Maximum specific growth rate of the nitrifiers at the reference temperature of 20°C (μ_{nm20})

(6) Average minimum and maximum temperatures (T_{min} and T_{max}) in the process.

Influent wastewater characteristics of lesser importance are:

(7) Unbiodegradable soluble COD fraction (f_{us})

(8) Unbiodegradable particulate COD fraction (f_{up}).

Influent characteristics normally not important in design are:

(9) Unbiodegradable soluble organic nitrogen fraction (f_{nu}) and

(10) Ammonia fraction of the TKN (f_{na}).

3. EFFECTS OF CHARACTERISTICS ON DESIGN

3.1 Influent COD and influent flow

The mean influent COD concentration, S_{ti},* and mean flow per day, Q, defines the mass COD load per day on the plant, $M(S_{ti})$, by

$$M(S_{ti}) = S_{ti}.Q$$

This COD mass consists of various fractions, as set out in Chapter 2, and these fractions are different for unsettled and settled municipal waste flows. However, to indicate the effect of the COD on the plant design, accept a specific waste flow influent. Then, for a specified sludge age, once $M(S_{ti})$ is known, theoretically the mass of sludge in the reactor, $M(X_v)$ or $M(X_t)$, and the mass of oxygen required daily for carbonaceous degradation, $M(O_c)$, also are known. The sludge age must be specified as the mass is very sensitive to the sludge age. Knowing the mass of sludge, the volume of the reactor is found from the specified mixed liquor concentration, X_v or X_t, i.e. the mass of sludge is "diluted" to the required concentration by providing the appropriate volume,

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*The mean influent COD, S_{ti}, is the *weighted* mean concentration; it is *not* the mean of the COD concentrations measured over the day on the influent. The magnitude of S_{ti} is found from measuring every hour, say, the COD, $S_{ti}(t)$, and flow, Q(t), and forming

$$S_{ti} = [\sum_{t=1}^{24} S_{ti}(t).Q(t)]/[\sum_{t=1}^{24} Q(t)]$$

If the wastewater is settled, S_{ti} refers to the measurements on the effluent from the primary settling tank.

$$V_p = M(X_v)/X_v \quad \text{or} \quad M(X_t)/X_t$$

Knowing the volume, one can now calculate, if so desired (it is not essential) the nominal hydraulic retention time, R_{hn}, of the reactor,

$$R_{hn} = V_p/Q$$

From a process design point of view the hydraulic retention time is of little interest: For two waste flows, having the same COD fractional constitution, provided $M(S_{ti})$ and X_v are the same for both, the volumes of the two plants and the oxygen demand per day will be identical irrespective of whether the first flow consists of a low S_{ti} and high Q and the second of a high S_{ti} and low Q. The nominal hydraulic retention time will differ, the first plant having a short and the second a long retention time respectively but this does not affect the degradation action, except insignificantly. The influent flow is important in the design of the settling tanks - for the same upflow velocity (overflow rate) in the secondary settling tank, the size for the first flow (high) will be larger than that for the second flow (low). Thus knowing only the COD load (and its fractional components), and the sludge age, the volume of the plant and the mean carbonaceous oxygen requirements can be estimated rapidly, also, the mass of sludge to be wasted per day. Knowing the mean flow, the size of the settling tanks can be estimated. Once these basic estimates are available, the effects of cyclicity in the flow and load on the peak carbonaceous oxygen demand and peak flow through the settling tank, then can be superimposed.

It was stated above that the mass of sludge, $M(X_v)$, depends on $M(S_{ti})$ and the sludge age. As the sludge age increases so the $M(X_v)$ increases likewise, the mass being roughly proportional to the sludge age; this is illustrated in Fig 3.1 where the mass of sludge in the process per unit influent COD, for unsettled and settled "normal" municipal waste flows, are shown plotted versus sludge age. Consequently the longer the sludge age, the bigger the reactor volume required to deal with the same $M(S_{ti})$. In Fig 3.1

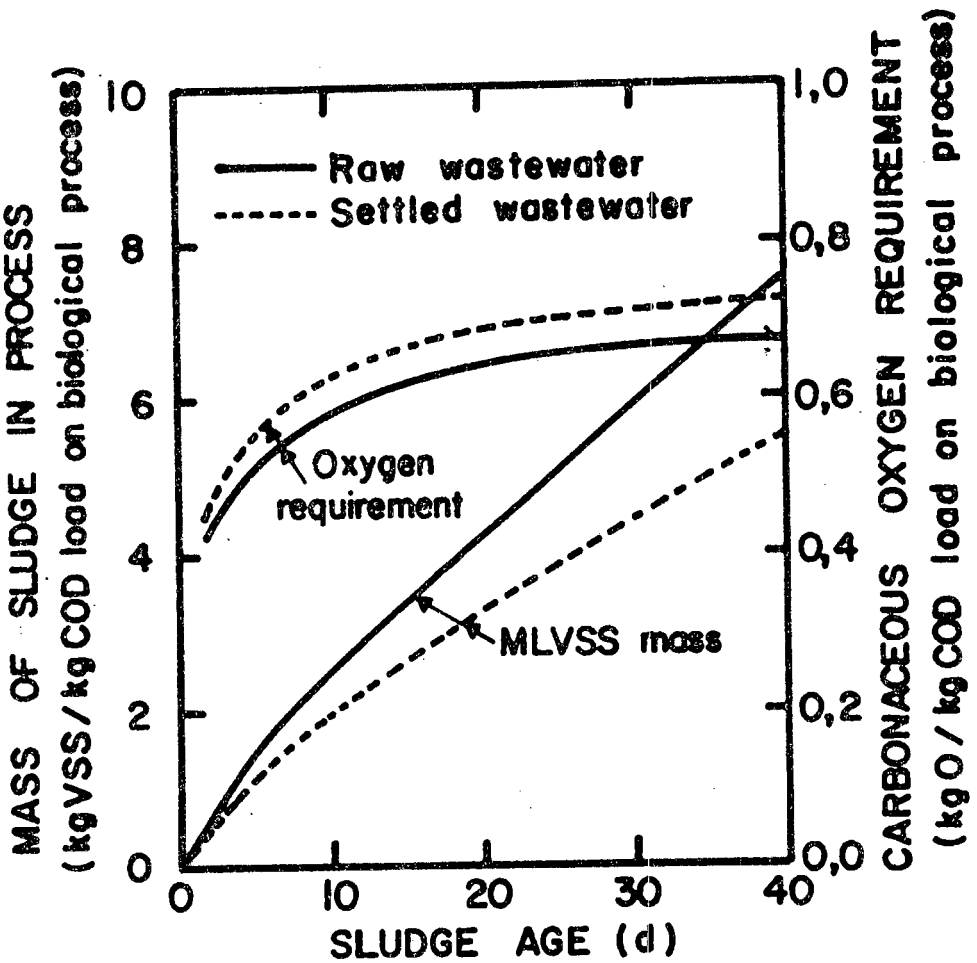

Fig 3.1 *Mass of volatile solids and mass of carbonaceous oxygen demand per day per kg COD load per day versus sludge age for settled and unsettled municipal waste flows.*

are shown plotted also the carbonaceous oxygen demands per unit COD input for settled and unsettled waste flows. As for $M(X_v)$ the respective magnitudes of $M(O_c)$ do not differ greatly between settled and unsettled wastes per unit influent COD. The difference arises principally from the fraction of unbiodegradable particulate COD, f_{up}, in the two wastes being higher in unsettled than in settled waste. However the total masses of sludge and carbonaceous oxygen demands for the two flows will differ appreciably because approximately 40% of the COD is removed in the primary settling tanks.

3.2 Influent TKN, μ_{nmT} and Temperature

In the discussion above, to calculate the sludge mass it was stated that the sludge age must be specified. Selection of the sludge age probably is the most important decision the designer must make, particularly when the objective includes nutrient removal. If removal of carbonaceous material only is required, the sludge age can be quite short; three days will be enough for COD removal - the sludge age selected is dependent more on the expected settleability of the sludge than on the COD removal. If nitrification only is required the sludge age must be sufficiently long to allow the nitrifying organisms to grow *and* metabolize virtually all the available nitrogen. If denitrification is required in addition to nitrification, a fraction of the sludge mass must be kept unaerated to denitrify the nitrate generated. As the nitrifiers are obligate aerobes, this implies that in a nitrification-denitrification plant the sludge age must be increased above that where nitrification only is required, to ensure that the aerobic sludge age is still adequate for nitrification.

The maximum specific growth rate constant of the nitrifiers, μ_{nm}, defines the minimum aerobic sludge age for the initiation of nitrification. This minimum sludge age must be increased by a further 25 percent to ensure that nitrification is near complete. Now μ_{nm} tends to be specific to the waste flow and can range from 0,30 to 0,65/day at 20°C. Also, μ_{nm} is very sensitive to temperature, the value halving for every 7 degC drop in temperature. The

"aerobic" sludge age is given by $1/\mu_{nm}$; it is clear therefore that, in a nitrification plant, a low μ_{nm} value for the waste flow coupled with a low temperature during the winter, will require a long sludge age to ensure efficient nitrification throughout the year. In nitrification-denitrification plants the process sludge age needs to be increased further to accommodate the effects of the unaerated fraction of the sludge mass. These factors in combination can cause that whereas a sludge age of 4 days for a $\mu_{nm} = 0,3$ at 20°C will be adequate theoretically for a purely nitrifying aerobic plant, for an nitrifying-denitrifying plant with $\mu_{nm20} = 0,3$, $T_{min} = 12°C$ and an unaerated sludge mass fraction of 0,5, the minimum process sludge age will be about 15-20 days to ensure a high efficiency of nitrification.

Provided the sludge age is adequate, the mass of nitrate formed by a process is given by the mass of TKN in the influent minus the mass of nitrogen incorporated in the sludge mass wasted every day. This gives the *nitrification capacity* of the plant (usually expressed as nitrate formed/unit flow). The higher the TKN concentration in the influent so, in general, the higher the nitrification capacity - we can form the rough rule that the nitrification capacity is proportional to the TKN concentration in the influent.

3.3 Readily Biodegradable COD, Slowly Biodegradable COD

3.3.1 Nitrogen removal

In the previous section it was mentioned that a fraction of the process sludge mass must be unaerated to denitrify the nitrate generated in the aerobic fraction, but the magnitude of this unaerated fraction was still undetermined. It is the intent now to describe qualitatively how this unaerated fraction is determined and how the influent characteristics affect the determination.

In the absence of oxygen, nitrate serves as an electron acceptor. With oxygen, the process designer has the problem of determining the oxygen demand for known COD load; in denitrification the problem is to determine the COD to denitrify a known mass of nitrate. The COD for denitrification comes from three sources (1) influent readily biodegradable soluble COD, (2) influent slowly biodegradable particulate COD and (3) particulate COD derived from the death of organisms. Usually (2) and (3) are lumped together in formulating the reduction of nitrate.

In the nitrification-denitrification process because the same sludge mass generates the nitrate and denitrifies it (called the single sludge process), the sludge mass normally is subdivided into two reactors in series, the one aerated (to nitrify) and the other unaerated (to denitrify).* Two basic configurations have been developed, the Modified Ludzack-Ettinger (MLE) configuration, Fig 3.2 and the Wuhrmann configuration Fig 3.3 . In the MLE configuration, the first reactor is left unaerated, the second is aerated. The nitrate generated in the second reactor is transferred to the first via the underflow and an inter-reactor (internal) recycle. In the Wuhrmann configuration the nitrate is generated in the first reactor and transferred by the normal serial flow to the second unaerated reactor - an internal recycle is not required, the only recycle being the underflow recycle to transfer the sludge from the secondary settling tank back to the first reactor.

The denitrification action can best be explained by considering the unaerated reactors as plug flow reactors. (This can be shown to provide valid explanation also for completely mixed reactors). In the unaerated reactor of the MLE configuration (called the primary anoxic reactor), the denitrification takes place at two simultaneously occurring rates, the first due to the influent readily biodegradable COD, the second due to the particulate COD derived principally from the influent, see Fig 3.4(a). The first rate is very fast, the reaction being complete in 6 to 20 minutes and it utilizes all the readily biodegradable COD. The second rate is slower, at about 1/7th of the first rate, and continues for the total time in the reactor. In the unaerated reactor of the Wuhrmann configuration, (called the secondary anoxic reactor), a single denitrification rate is observed, due principally to the slowly biodegradable particulate COD derived from death of the

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*Other processes, in which the sludge is sequentially aerated and left unaerated, also have been proposed and built, either sequentially in time in a single completely mixed reactor or sequentially in space as, for example, in the Carrousel system.

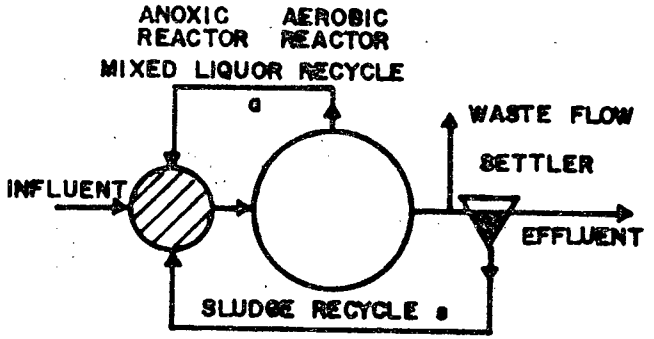


Fig 3.2 *Modified Ludzack-Ettinger nitrification -denitrification activated sludge process.*

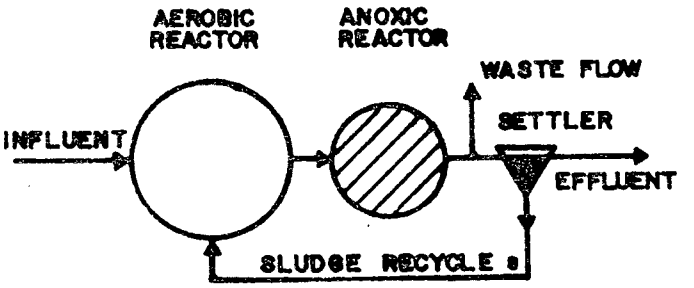
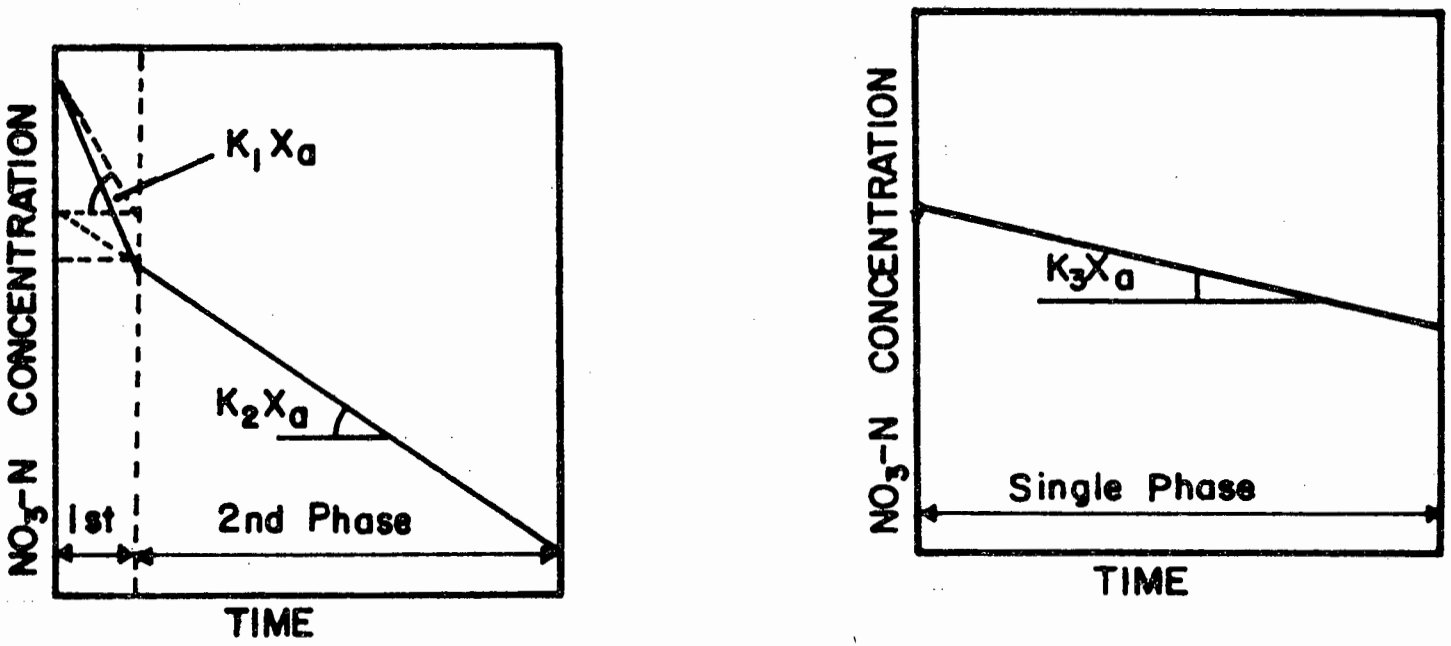


Fig 3.3 *Wuhrmann nitrification-denitrification activated sludge process.*



(a) Primary anoxic

(b) Secondary anoxic

Fig 3.4 *Denitrification time behaviour in plug flow anoxic reactor, (a) primary anoxic and (b) secondary anoxic reactors.*

organisms, [Fig 3.4(b)]. This source of COD becomes available at a low rate and the denitrification rate accordingly is low, about 2/3 that due to particulate COD in the MLE primary anoxic reactor.

The nitrate removal can be expressed either as total mass removed per day or as mass removed per litre of flow, i.e. as a concentration relative to the flow mg $\Delta(NO_3\text{-}N)/\ell$ flow.
The latter method is the most convenient because it allows ready comparison with the TKN concentration in the influent flow, mgTKN/ℓ flow.
We have stated that the removal is due to the complete utilization of the readily biodegradable COD and the partial utilization of the biodegradable particulate COD. The denitrification achievable due to the latter can be formulated in terms of a denitrification rate constant, K, the *active* mass of sludge generated per litre of influent and the fractional mass of the process sludge contained in the specific anoxic reactor, as follows: (See Chapter 6, Section 4).

In the primary anoxic reactor

ΔN_1 = C (mass of readily biodegradable COD per litre of influent)
+ K_2 (mass of active sludge generated by one litre of influent) x (mass fraction of sludge in the primary anoxic reactor) (1)

In the secondary anoxic reactor

ΔN_3 = K_3 (mass of active sludge generated per litre of influent)
x (mass fraction of sludge in the secondary anoxic reactor) (2)

The values of K_2 and K_3 have been determined experimentally and found to remain virtually constant for sludge ages between 10 and 30 days, at a fixed temperature. This is also indicated by simulation using the general activated sludge model of Dold, Ekama and Marais (1980) as extended to include denitrification by van Haandel, Ekama and Marais

(1981). The two equations developed above, expressed in technical terms are for primary and secondary anoxic reactors respectively

$$\Delta N_1 = f_{bs} (1-f_{up} -f_{us}) S_{ti}/8,6$$

$$+ K_2 \frac{Y_h R_s}{1 + b_h R_s} S_{ti} (1-f_{us} -f_{up}) \frac{R_{hn1}}{R_{hn}} \qquad (3)^*$$

$$\Delta N_3 = K_3 \frac{Y_h R_s}{1 + b_h R_s} S_{ti} (1-f_{us} -f_{up}) \frac{R_{hn3}}{R_{hn}} \qquad (4)^*$$

R_{hn1}/R_{hn} and R_{hn3}/R_{hn} are the ratios of the nominal retention times of the primary and secondary anoxic reactors respectively with respect to the total. The ratios respectively are equal to the primary and secondary anoxic sludge mass fractions. Here as for aerobic biological degradation, the nominal retention is not the basic parameter even though one may formulate the equations to include it. From Eqs (3) and (4) the denitrification potential is a function of the influent COD, S_{ti} but is approximately so only being modified by the magnitude of the unbiodegradable fractions of the influent COD, f_{us} and f_{up} .

In Eq (1), all the readily biodegradable COD is utilized; the denitrification attained from this source in the influent is very effective and constitutes about 50% denitrification achieved in "normal" municipal wastewater. The removal due to the particulate biodegradable COD typified by K_2 and K_3 in Eqs (1) and (2) *inter alia*, is directly proportional to the anoxic sludge mass fractions of the respective anoxic reactors (i.e. f_{x1} and f_{x3}). These fractions cannot be increased *ad lib*; for a fixed sludge age the magnitude of the sum of these two fractions is subject to the proviso that efficient

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*These equations are for illustrative purposes only, the meaning of the symbols can be found in Chapters 4 to 6.

nitrification must be maintained and this in turn is fixed by the aerobic sludge age. In this way there is an upper limit to the sum of anoxic sludge mass fractions which limits the nitrate removal achievable. Furthermore because K_3 is roughly 2/3 of K_2, the nitrate removal due to K_3 in the secondary anoxic reactor per unit volume is only about 2/3 as effective as that in the primary anoxic reactor so that per unit sludge mass fraction the primary anoxic reactor is more efficient than the secondary anoxic reactor.

The nitrate removals, ΔN_1 and ΔN_2, are called the *denitrification potentials* of the respective reactors. The term *potential* is used because in the primary anoxic reactor (as in an MLE process), for example, the denitrification potential can be achieved only if sufficient nitrate, equal to the potential, is recycled to this reactor - if less is recycled the full potential of the reactor is not realized and the *denitrification performance* (or *denitrification capacity*) is less than the denitrification potential. When the performance is less than the potential then the performance can be increased by increasing the recycle. Now the recycle contains dissolved oxygen in addition to nitrate, and the oxygen utilizes the COD preferentially; in consequence, recycle ratios in excess of 4 to 6 usually do not significantly improve the performance, but even can cause a *decrease* in performance due to the high mass of D.O. transported to the anoxic reactor via the recycle flow. If more nitrate is recycled than that defined by the potential, only the potential value is removed, the excess is returned from the anoxic reactor to the aerobic reactor; in such a situation the recycle can be reduced appropriately without affecting the nitrogen removal by the process.

The combined primary and secondary anoxic sludge mass fraction i.e. the total unaerated sludge mass fraction, cannot be increased *ad lib.*, for two reasons:

(1) Nitrification requires a minimum aerobic sludge age and to preserve this, as the unaerated mass fraction is increased so

also the process sludge age must be increased to preserve the minimum aerobic sludge age; increasing the sludge age, however, increases the total mass of sludge and hence the total volume of the reactor system. Furthermore, any increase has a relatively small effect on nitrate removal because the increase contributes to denitrification only through the K_2 or K_3 components and these are relatively inefficient. Practically, for South African conditions, the upper limit to a sludge age appears to be about 30 days.

(2) When the nitrification rate is high the aerobic sludge age can be small so that with a long sludge age it would be possible to have a large unaerated sludge mass fraction. Experimental data, supported by simulation studies, show that for sludge ages between 20 and 30 days, if the unaerated fraction of a process increases above about 70% at 20°C and about 50% at 12°C the time available for aerobic degradation is insufficient to process all the particulate influent biodegradable COD and the process acquires a degradation pattern still ill understood. Consequently for design under South African conditions for sludge ages of 20 to 30 days, the unaerated mass fraction should not exceed about 55 to 60%.

We have noted earlier that the denitrification potentials are approximately proportional to the influent COD concentration, S_{ti}. Now previously it was pointed out that the nitrification capacity is approximately proportional to the influent TKN. Consequently the TKN/COD ratio of the influent is a good parameter in terms of which to assess process nitrification-denitrification behaviour because it gives approximately the ratio of the nitrate generated to the denitrification potential. Now accepting that

1) μ_{nm} will vary around 0,4/d,

2) the sludge age is in the range 20 to 30 days,

3) "normal" municipal wastewater flows contain roughly readily biodegradable COD fractions of about 20% with respect to the total influent COD,

4) the internal recycle ratio is limited to a maximum of 6:1,

5) the minimum winter temperature is 14°C,

it would appear that for these conditions, if the influent TKN/COD is greater than about 0,10, the denitrification potential is such that it is not possible to denitrify all the nitrate generated even if all the unaerated fraction of the process is located in the primary anoxic reactor. Consequently in this situation the MLE process is the most efficient. If the influent TKN/COD ratio is less than about 0,09 then complete denitrification is possible. Even if complete denitrification is possible this cannot be accomplished by using an MLE process only for the following reason:

Say the steady state nitrate concentration in the aerobic reactor is N mg/ℓ, if an internal recycle ratio of a is imposed and an underflow recycle ratio of s then (a+s)/(a+s+1) of this nitrate is recycled and 1/(a+s+1) goes out with the effluent. To deal with the 1/(a+s+1) fraction a secondary anoxic reactor needs to be incorporated also in the process, to give the Bardenpho process first proposed by Barnard, 1973 (Fig 3.5). Of course the secondary anoxic reactor per unit volume is not as efficient as the primary because $K_3 < K_2$ so that the denitrification potential for the same unaerated total mass fraction will be lower than for an MLE process only, but this must be sacrificed and is the reason why complete denitrification is achievable only for a TKN/COD $\leq$ 0,09 instead of 0,10. This significant reduction in the upper limit of the TKN/COD is principally because the a-recycle should not be increased above a = 6 (to limit the feedback of oxygen to the primary anoxic reactor). If the oxygen in the recycle could have been reduced to zero then very high a-recycles could be utilized and it might not be necessary to employ a secondary anoxic reactor.

As the TKN/COD ratio decreases below 0,09 so the size of the primary anoxic reactor may be decreased and the second anoxic reactor increased in order to maintain a low recycle, illustrated in Fig 3.6.

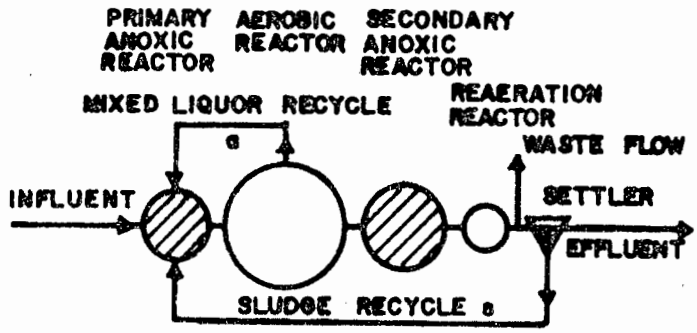

Fig 3.5 *Bardenpho process for biological nitrogen removal - a combination of the modified Ludzack-Ettinger and Wuhrmann processes.*

3.3.2 Excess Phosphorus removal

There is considerable support for the view that under certain conditions some species of organisms, for example, the *Acinetobacter spp*, can take up phosphorus in excess of its metabolic requirements. Some of the acinetobacter species are obligate aerobes, others can utilize nitrate as electron acceptor. The species is slow growing with rather specific requirements to the type of nutrient it can utilize; it can utilize, for example, many of the lower fatty acids, but not sugars, such as glucose. Because it is slow growing, in aerobic systems, with mixed cultures of organisms, its growth is suppressed by faster growing organisms, because the faster growing organism utilizes most of the substrate and eventually dominates over the slow growing ones. This is the reason why it is not easy to find evidence of acinetobacter in purely aerobic processes.

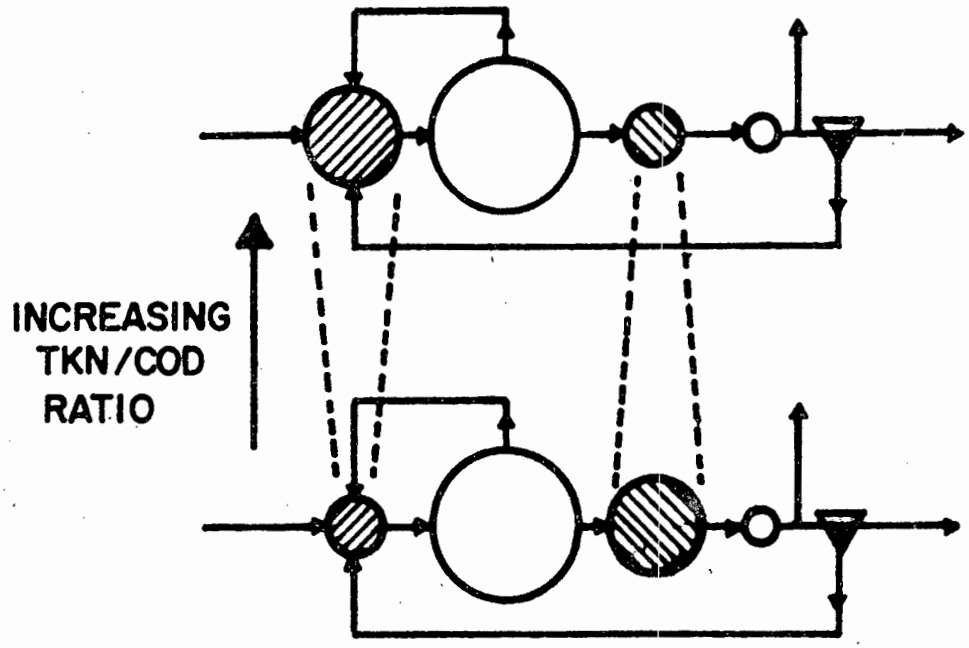

Fig 3.6 *Effect of TKN/COD ratio on relative sizes of primary and secondary anoxic reactors in the Bardenpho process.*

From the discussion above, how then does it happen that the poly-P organism proliferates in some systems containing unaerated fractions? Assume that the organism already contains some excess phosphate. This phosphate is present as the radical PO_4^- but bound together to form polyphosphate chains. The bonds between the radicals in the chain contain appreciable energy. If the acinetobacter is discharged to an anaerobic reactor (i.e. a reactor that has neither nitrate nor oxygen present), in which substrate is present suitable for growth of *Acinetobacter spp*, it breaks down some of the bonds in the polyphosphate chain, releasing phosphate radicals to the surrounding liquid. The bond energy thus released is utilized to absorb, complex and store the substrate in the organism - we say it sequesters the substrate. In contrast, in the anaerobic zone, because no external electron acceptor (oxygen or nitrate) is available, the non poly-P organisms cannot utilize the substrate. On leaving the anaerobic zone and entering an anoxic zone (with nitrate present) or an aerobic zone (with oxygen present), the poly-P organism now has electron acceptors available and metabolizes the stored substrate sequestered for itself in the anaerobic zone i.e. it can grow without being in competition with the non poly-P organisms for the balance of the energy still available in the surrounding medium.

In the anoxic and aerobic zones the poly-P organisms, beside using the sequestered substrate for growth, also use it to take up phosphate radicals (PO_4^-) from the surrounding medium, again to form phosphate chains for use subsequently when returned to the anaerobic zone. Thus, by having the propensity to store polyphosphate the acinetobacter and other poly-P organisms have a positive advantage over the non poly-P organisms to obtain energy for themselves in the apparently inhospitable anaerobic reactor. This explains the apparently anomolous growth response of the poly-P organisms.

The behaviour of the poly-P organisms in the anaerobic reactor is not yet well understood but a summary of the behaviour appears to be as follows: When a substrate is added that can be utilized *directly* by the poly-P organisms, such as acetate or butyric acid, the release of P (to obtain energy for sequestering

the substrate) is very rapid, and the release is proportional to the mass of substrate added. Also, the net removal of P from the anaerobic-anoxic-aerobic system increases as the substrate added increases, but insufficient data has been collected to express these responses quantitatively.

When sewage is added to the anaerobic reactor the behaviour differs in two aspects from that when acetate is added: (1) only a fraction of the COD added is implicated in the P release and P removal, (2) the rate of P release is significantly slower with sewage than with acetate addition and the release is of a different kinetic order.

(1) The influent COD that induces P release seems to be associated with the readily biodegradable COD fraction. It has been observed consistently in laboratory scale processes that the release and removal of P increases and decreases as this fraction increases and decreases (see Fig 3.7) although it is not yet clear, and highly unlikely, if all the readily biodegradable COD is implicated in this action.

With regard to the particulate biodegradable COD, this fraction appears to have little effect on P release. This is not an unreasonable conclusion because the particulate COD requires adsorption, storage and extracellular breakdown prior to absorption by the organisms; even under aerobic conditions the rate of metabolism of the particulate COD is only at 1/7 to 1/10 the rate at which readily biodegradable COD is metabolized, Dold, Ekama and Marais (1981).

(2) The slower rate of P release with sewage addition compared to that with acetate addition seems to indicate that the substrate suitable for P release becomes available indirectly to the poly-P organisms. This is further supported by the observation that whereas with acetate addition the P release appears to be zero order with respect to acetate concentration, (Fig 3.8), with sewage addition the release appears to conform to a first order reaction; in a plug flow anaerobic reactor receiving sewage the rate of release is high initially but dies away steadily

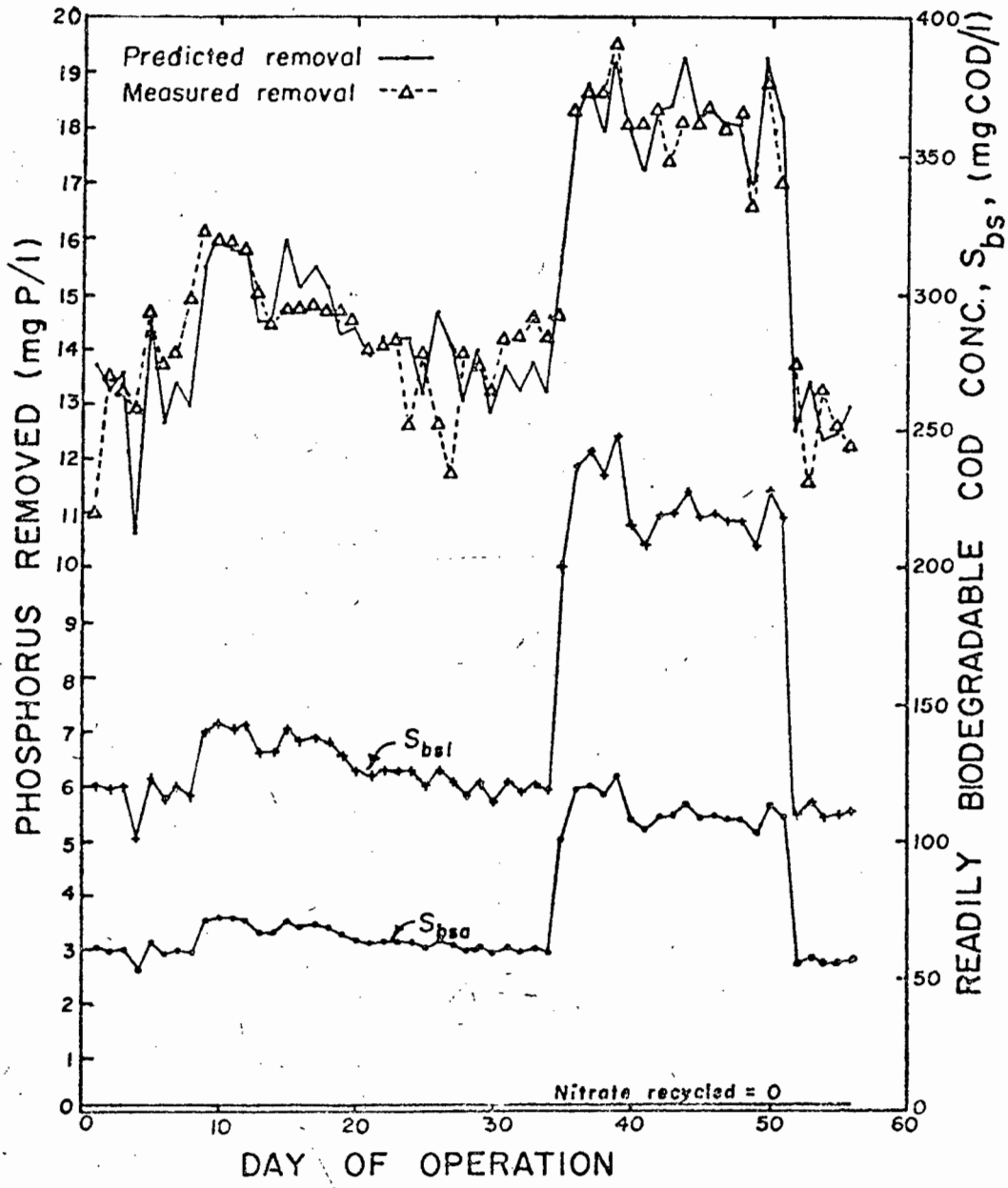

Fig 3.7 *Experimental data showing the strong dependance of excess P removal (ΔP) with readily biodegradable COD in the influent (S_{bsi}).*

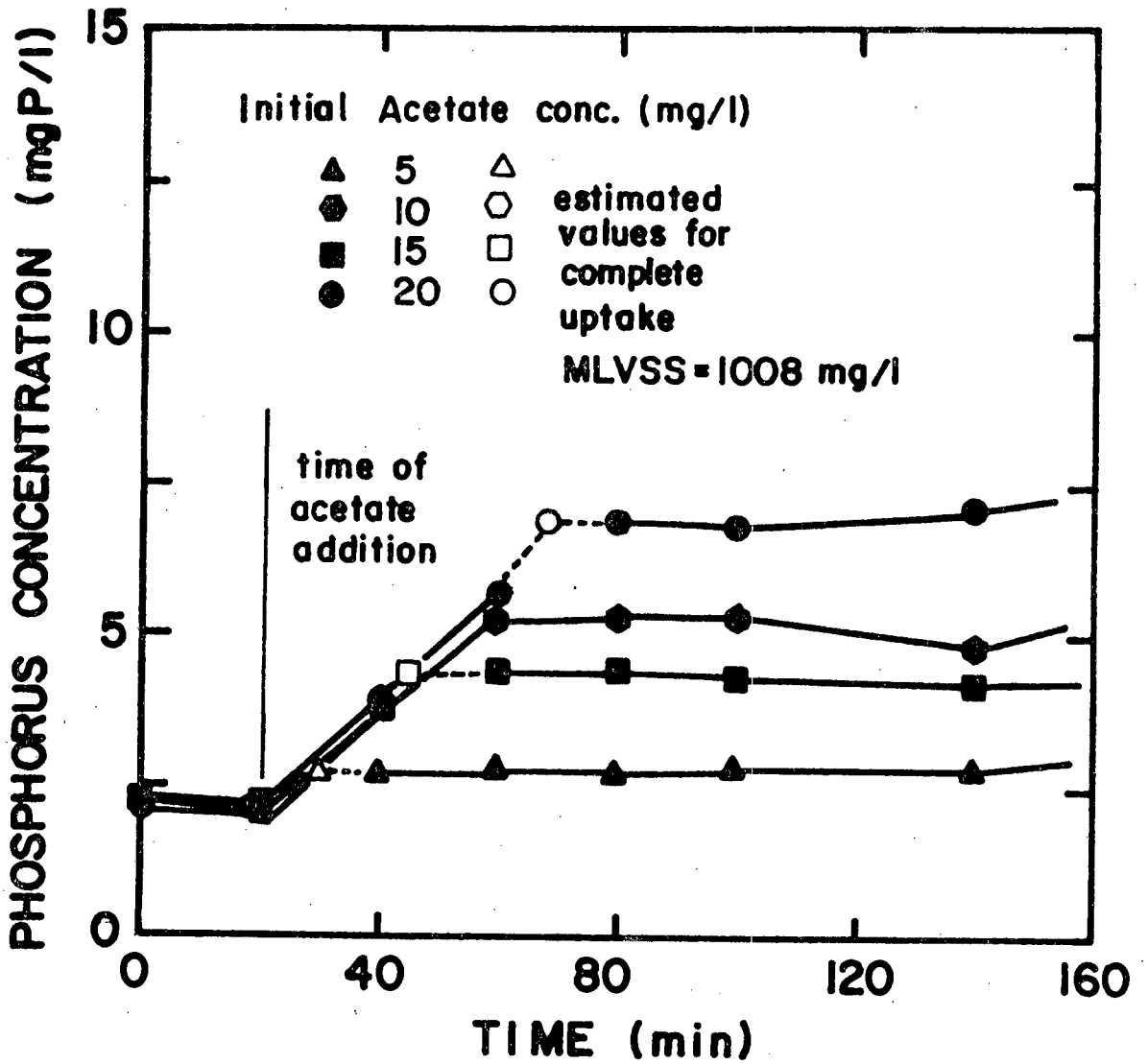

Fig 3.8 *Phosphorus release in a batch anaerobic reactor with different concentrations of acetate added. Note the magnitude of the release is proportional to mass of acetate added but the rate of release is independent of the acetate concentration.*

along the reactor until it is virtually zero. This is also indicated in a series system of anaerobic reactors (Fig 3.9). The first order nature of the reaction in the series system is verified by plotting the log (release/reactor) versus the cumulative retention time, to give a linear plot, (Fig 3.10). Comparison between the release in a plug flow reactor and a completely mixed reactor also shows that for the same anaerobic mass fraction if the mass fraction is so small that all the P is not released in the plug flow reactor, the release in the completely mixed reactor is less than in the plug flow one, a behavioural pattern in conformity to that expected where a first order reaction controls.

According to the observed behaviour described above, at sludge ages about 20 to 25 days, the anaerobic mass fraction of a completely mixed reactor should be about 0,2 to ensure that 90% or more of the P is released; if it were a plug flow reactor the mass fraction needs to be about 0,15 to give the same percentage release. Because the release rate is first order there is little to be gained by making the anaerobic mass fraction greater than about 20%. Mass fraction of 10 percent or less again will be too small allowing only about 50 to 60% of the potential release to take place. Then again, subdividing the anaerobic reactor into say two reactors in series gives improved usage of the anaerobic reactor mass fraction and requires a mass fraction of about 15% to give the same release as a completely mixed reactor of 20%. These fractions apply only for sludge ages of 20 days and longer.

The reasons for the different responses observed with acetate and sewage readily biodegradable COD additions are not yet clear but the following explanation could be valid: Most of the fractions of readily biodegradable COD, apparently, are not in a chemical form suitable for utilization by the poly-P organisms. In the anaerobic zone the non poly-P organisms, for *survival*, because no external electron acceptors are available, partially utilize the readily biodegradable COD, via the Embden-Meyerhof or other equivalent pathways, to generate a small amount of energy, by creating internal or

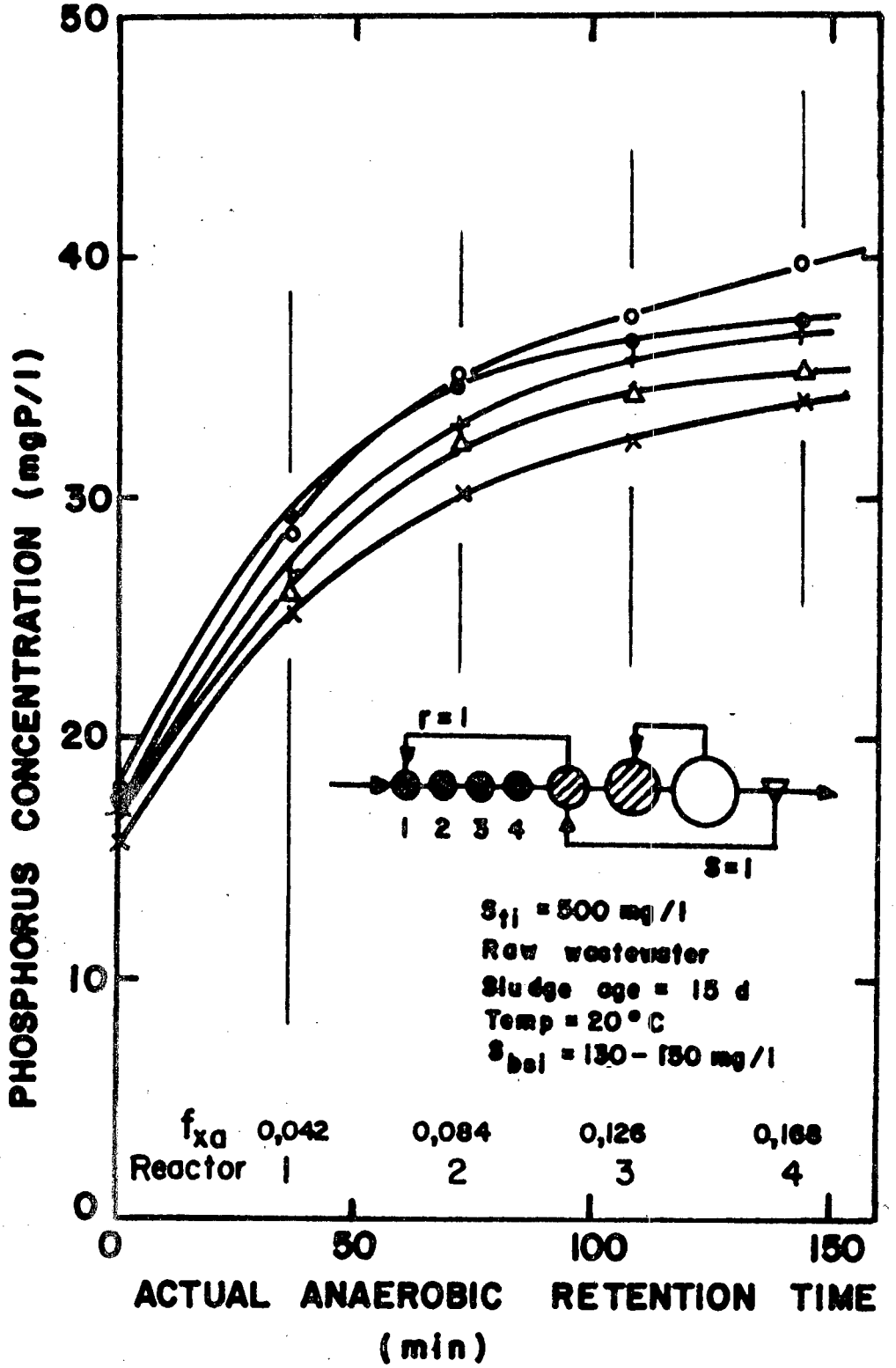

Fig 3.9 *Phosphorus concentration in a four in series anaerobic reactor system, in a modified UCT process, receiving unsettled municipal sewage influent.*

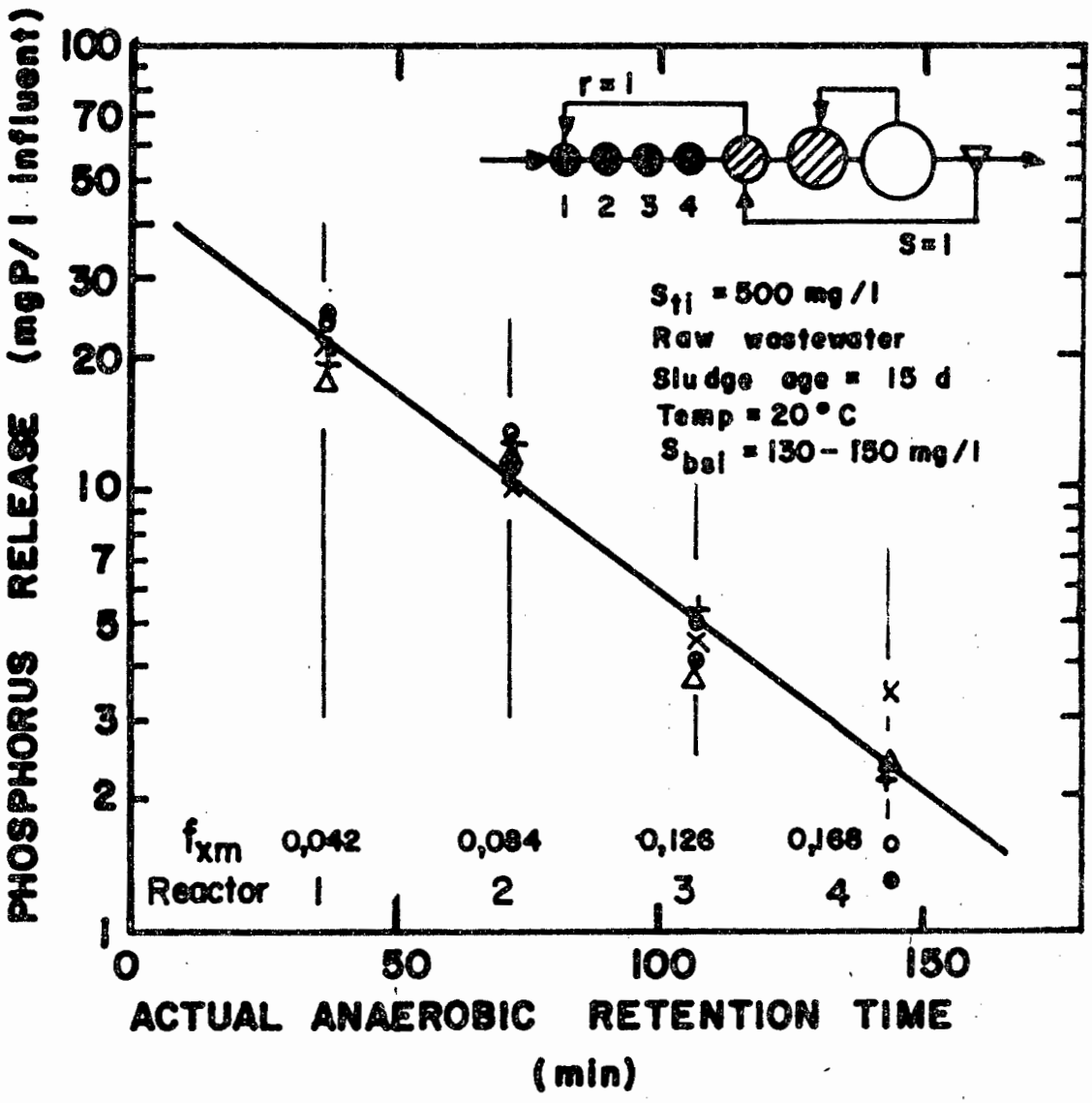

Fig 3.10 *Phosphorus release per reactor in a four in series anaerobic reactor system in a modified UCT process receiving unsettled municipal sewage influent (see also Fig 3.9).*

endogenous electron acceptors: The outcome of this action is a breakdown of the original COD molecules to lower fatty acids and other similar forms. These are rejected by the organism and become available to the poly-P organisms for sequestration. Thus, where substrate is present in a form unavailable to the poly-P organism, the presence of non poly-P organisms can modify some of the COD fractions to forms suitable for use by the poly-P organisms. The kinetics of this transformation will govern the kinetics of sequestration by the poly-P organisms because the COD breakdown is the rate limiting step. The non poly-P organisms are, in terms of this hypothesis, essential to the growth of the poly-P ones.

3.3.3 Implication on process development

The rationalization of the poly-P behaviour leads to a number of conclusions that are of significance to designers of P removal processes:

(1) In terms of the hypothesis set out above, the generation of the lower fatty acids by acid digestion of primary settling tank underflow, as proposed and implemented by the Municipality of Johannesburg, makes good sense and merits serious research attention.

(2) Any external electron acceptor entering the anaerobic reactor, like nitrate or oxygen, will be utilized immediately by the non poly-P organisms acting on the readily biodegradable COD and thereby reduce the COD concentration available for the generation of substrate suitable for sequestration by the poly-P organisms.

(3) The fact that the whole sequestration action is slow means that adequate anaerobic mass must be made available to process as much as possible of the readily biodegradable COD source. However because the reaction is first order it also implies that there is little merit in enlarging the anaerobic mass *ad lib.*, each increase giving a decreasing return on the previous increase. Also, series anaerobic reactors are more efficient and hence smaller anaerobic mass is necessary, to achieve the same effect than with a single completely mixed anaerobic reactor.

With regard to design implications, the basic requirement in a design is to provide an anaerobic zone which receives the influent containing the COD fraction and so becomes available, directly or indirectly, to the poly-P organisms for sequestration. This zone must be large enough to allow the sequestration action to be as near complete as possible in order to obtain maximum effect. Furthermore, the zone should not receive any form of the external electron acceptors (nitrate, nitrite or dissolved oxygen) as these cause the fast growing non poly-P organism to utilize the substrate before it can be sequestered by the poly-P organism.

The first explicit process configuration, in which an anaerobic reactor was proposed, was due to Barnard* (1976). He accepted the Bardenpho process (Fig 3.5) as the basic configuration to nitrify and denitrify. A fraction of the primary anoxic reactor was isolated to serve as an anaerobic reactor. This reactor was placed at the head of the process and received the underflow recycle and the influent flow (see Fig 3.11). The reasoning behind this configuration was that the Bardenpho section of the process would give complete nitrification and denitrification so that the underflow would contain little or no nitrate, in this fashion allowing optimal conditions in the anaerobic reactor and maximum release of P. The process configuration has been variously called the Modified Bardenpho, Phoredox or 5 stage Phoredox process.

In assessing the functioning of the Phoredox process, the reservation of a portion of the unaerated mass fraction to the anaerobic reactor concomitantly reduces the denitrification potential of the process. Thus, compared to the Bardenpho process for the same total unaerated mass fraction, the Phoredox has a lower denitrification potential. Consequently the maximum TKN/COD ratio the Phoredox process can denitrify completely is reduced. For a "standard" raw

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*The basis for proposing the anaerobic reactor, by Barnard, differs fundamentally from the hypothesis suggested in the previous sections. He suggested that the *redox potential* need to be lowered sufficiently to induce P release. He noted the adverse effect on P removal by nitrate discharged to the anaerobic reactor but suggested that this arose from the nitrate limiting the depression of the redox potential. These aspects are dealt with in greater detail in Chapter 7.

sewage influent i.e. 20% of the influent COD is readily biodegradable, at sludge ages of approximately 20 days, maximum unaerated mass fraction of 0,55 and an anaerobic mass fraction of 0,15, it would seem that the maximum TKN/COD ratio for complete denitrification should not exceed 0,08. For settled sewage the readily biodegradable COD is higher ≅ 25% of the total influent COD and the maximum TKN/COD ratio is about 0,09. This ratio is very dependant on the fraction of readily biodegradable COD because this fraction contributes significantly to the denitrification. Consequently the values given here are relative ones only - it is important to estimate the true readily biodegradable fraction experimentally.

As the TKN/COD ratio increases from low values, so it will be found that the relative volumes of the primary and secondary anoxic reactors change accordingly. To achieve optimum denitrification response at low TKN/COD ratios the primary reactor is small and the secondary reactor large; at high TKN/COD ratios, near or at the maximum allowed, theprimary reactor is large and the secondary very small.

Should the TKN/COD ratio exceed the maximum, nitrate will appear in the effluent. In the Phoredox process this nitrate is recycled in the underflow to the anaerobic reactor where it utilizes preferentially some, or all (depending on the concentration of nitrate) of the readily biodegradable COD, thereby recucing the magnitude of the COD available for sequestration by the poly-P organisms. Now the concentration of nitrate in the underflow recycle is the same as that in the effluent and 1 mg (NO_3-N) removes 8,6 mg readily biodegradable COD, consequently, a concentration of 5 mg/ℓ (NO_3-N) in the underflow with a recycle ratio of 1:1 will remove 43 mg of this COD fraction which, for an influent of 500 COD/ℓ will reduce the readily biodegradable COD from approximately 100 to 60 mg/ℓ. The only operational means for reducing the mass of nitrate transferred to the anaerobic reactor is to reduce the underflow recycle ratio but this procedure has only limited possibilities because low recycle ratios may give rise to difficulties eith the secondary settling tank - at low recycles the sludge mass builds up in the tank and

may cause failure of the tank when the SVI is high, or loss of sludge in the effluent may occur from rising sludge due to denitrification in the sludge mass.

The principal difficulty with the Phoredox configuration, under high TKN/COD ratios,arises from the fact that the anaerobic reactor performance is dependent on the nitrate in the effluent. To make the anaerobic reactor independent of the effluent nitrate, the University of Cape Town (UCT) process configuration was developed, Fig (3.12). The basic denitrification configuration is the Modified Ludzack-Ettinger process (Fig 3.2). The anaerobic reactor is, like the Phoredox, placed at the head of the works but the recycle flow to this reactor,(the r-recycle), is taken from the primary anoxic reactor. By regulating the main internal recycle from the aerobic to the anoxic reactor, the a-recycle, so that the denitrification potential of the primary anoxic reactor is not exceeded,a nitrate free effluent is assured to the anaerobic reactor.

In the UCT process, if, say, an r-recycle of 1:1 is used the concentration in the anaerobic reactor is half that in the rest of the plant and to get the required anaerobic mass fraction the volume of this reactor must, in consequence, be increased to twice the volumetric size of that in the Phoredox for the same anaerobic mass fraction. The main advantage of the UCT process is that by operational means,the anaerobic reactor can be made independent of the nitrate in the effluent, and this can be maintained up to a TKN/COD ratio of about 0,14. As an alternative to the Phoredox process, at low TKN/COD ratios, i.e. TKN/COD < 0,08, the UCT process is also satisfactory although the nitrate removal will not be as high as in the Phoredox as it is not possible ever to get zero nitrate in the effluent from a UCT process.

To overcome the need for explicit control of the a-recycle, the Modified UCT process was developed, (Fig 3.13). In this process the primary anoxic reactor is divided into two fractions, the first having an anoxic mass fraction of about 0,1. The a-recycle is discharged to the second anoxic reactor and remains fixed at say 4:1 ratio irrespective of whether nitrate is recycled back to the aerobic

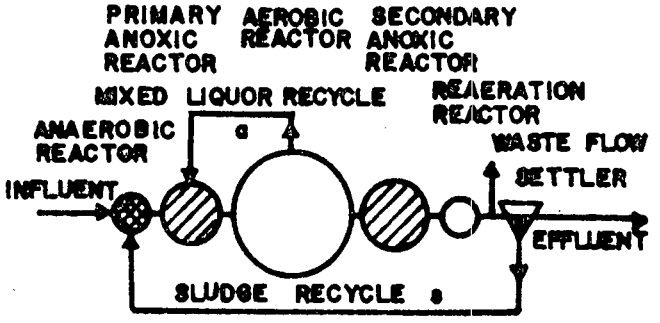

Fig 3.11 *Phoredox (or modified Bardenpho) process for nitrification-denitrification-biological excess phosphorus removal.*

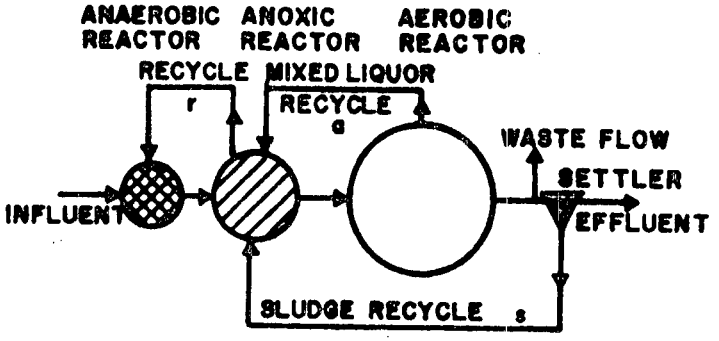

Fig 3.12 *University of Cape Town (CT) process for nitrification-denitrification-biological excess phosphorus removal.*

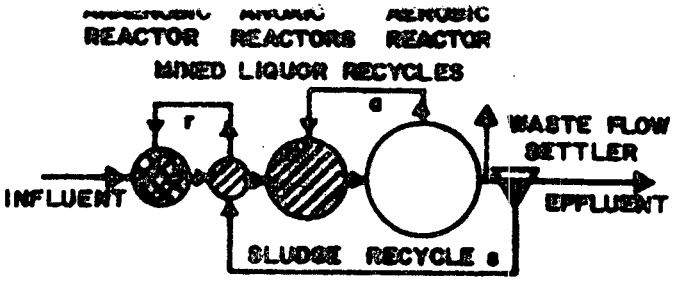

Fig 3.13 *Modified UCT process.*

reactor or not, provided the a-recycle ratio is so large that it brings enough nitrate to the second anoxic reactor to equal or exceed its denitrification potential. The underflow recycle (s-recycle) discharges to the first anoxic reactor, to reduce the nitrate to zero. By means of this configuration zero nitrate in the r-recycle can be maintained for TKN/COD ratios up to about 0,11.

4. CLOSURE

There are numerous aspects and details in the design of nutrient removal plants that have not been dealt with in this short review - attention was focussed on the major aspects of a fundamental nature only. For details of design reference needs to be made to Chapters 4 to 7. Designs that conform to the recommendations laid down in these chapters, for treating normal municipal wasteflows, settled or unsettled, will have a high expectation of phosphorus removal of about 1,7 to 2 mgPO_4-P per 100 mg influent COD, i.e. a ΔP/COD of 0,017 to 0,02 mgP/mg influent COD. This removal ratio can vary, depending principally on the fraction of readily biodegradable COD in the influent. Should the influent P/COD concentration ratio exceed 0,017 to 0,02, very likely all the phosphorus will *not* be removed biologically from the wastewater and provision necessarily will have to be made for chemical precipitation of the remaining phosphorus; should the influent P/COD be *less* than 0,017 to 0,02, then very likely removals down to 0,5 mgP/ℓ can be achieved for a high proportion of the time.

The above biological P removal propensity in ΔP/COD forms an approximate basis for judging the performance of any designed plant. *The plant should not be assessed on the basis of the effluent P concentration only*, but on the ΔP per unit influent COD. If the ΔP/COD achieved is less than 0,017 to 0,02, the cause for the lower removal should be sought in the wastewater characteristics, process design or operation of the plant, or in combinations of these three. The results of such investigations would be of great value to research workers and designers in the endeavour to build plants that perform optimally.

5. REFERENCES

1. Dold P L, G A Ekama and G v R Marais (1980) "A general model for the activated sludge process", Prog.Wat.Tech., 12, 47-77.

2. van Haandel A C, G A Ekama and G v R Marais (1981) "The activated sludge process part 3 - single sludge denitrification, Water Research, 15, 1135-1152.

CHAPTER FOUR

CARBONACEOUS MATERIAL REMOVAL

by

G A Ekama and G v R Marais

1. INTRODUCTION

Basically all aerobic biological treatment processes operate on the same principles: the various treatment processes i.e. trickling filters, aerated lagoons, contact-stabilization, extended aeration, etc. differ only in the conditions under which the biological reactions are constrained to operate. The activated sludge process comprises the flow régime in the reactor, the sizes, number and configuration of the reactors, recycle flows, influent flow and other features incorporated either deliberately, or presemt inadvertently or unavoidable. Whereas the response of the organisms is in accordance with their nature, that of the process is governed by both the organism characteristics and the physical features that define the process.

The ecology of the suspended sludge mass in the reactors of the activated sludge processes is complex comprising numerous species of bacteria and many species of higher organisms that prey on the bacteria. Despite the complex nature of the ecosystem, it would appear that the kinetic behaviour of the process, insofar as it reflects the energy removal from the wastewater, can be modelled as if the system were governed by an equivalent or surrogate bacterial mass, having characteristics derived in part from the observed response of the treatment processes. It must be emphasised that this surrogate mass has characteristics very different from those of a pure bacterial culture. This point is mentioned because criticism of this approach has often hinged on the incompatibility of the behaviour of the equivalent bacterial mass with that observed in a pure bacterial culture.

In this chapter the basic kinetics of the carbonaceous material removal, and its incorporation in the process equations are briefly stated, and application to design is set out in detail. The design equations presented are for the steady state completely mixed single reactor activated sludge process. The steady state solution is of prime importance because (1) it forms the basis for preliminary design of any activated sludge process be it aerobic, anoxic-aerobic or anaerobic-anoxic-aerobic. (2) The relationships also are useful in indicating operational control procedures for the process.

If certain minimum conditions are imposed on the process, nitrification will occur. With nitrification the oxygen demand can show a considerable increase, of up to 40% more than that required for carbonaceous material oxidation. Nitrification is not dealt with in this chapter but is considered in detail in Chapter 5.

2. BIOLOGICAL KINETICS

When a heterotrophic organism population under aerobic conditions is brought into contact with biodegradable organic material* consisting of soluble readily biodegradable and particulate slowly biodegradable COD fractions (see Chapter 2), its response may be described qualitatively as follows:

(1) The soluble readily biodegradable COD passes directly through the cell wall and is metabolized at a high rate.

(2) The particulate slowly biodegradable COD is adsorbed onto the organisms and storage of COD takes place.This reaction is very rapid and effectively removes all the particulate and colloidal COD from the wastewater. The stored COD is broken down by extra-cellular enzymes and transferred through the cell wall and metabolized in the

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* Also called substrate or biodegradable COD.

same manner as the readily biodegradable COD fraction in (1) above. The rate of enzymatic breakdown is relatively slow and constitutes the limiting rate in the overall synthesis reaction, at about one tenth of the rate for the readily biodegradable COD.

(3) A fraction of the COD metabolized is converted into new cell material, the balance is utilized to generate energy to bring about the conversion and eventually, is lost as heat. The energy is generated by supplying an electron acceptor,oxygen,so that the oxygen utilized is directly related to the COD lost. There is strong experimental evidence that the fraction of COD converted to metabolic material is constant with respect to the COD utilized, Payne (1971). This fraction is called the specific growth yield coefficient, Y_{COD} (mg COD/mg COD). Usually the coefficient is expressed in terms of the volatile solids formed per unit of COD utilized, Y_h, (mg VSS/mg COD) and is related to Y_{COD} by Eq. (1.6), i.e. $Y_h = Y_{COD}/f_{cv}$.

(4) Concomitantly with (3) above, but distinct from it, there is a *net* loss of live mass called endogenous mass loss. Not all the live mass that disappears *per se* is lost as energy, a fraction remains (17 to 20 percent, McKinney and Symons, 1964) as unbiodegradable organic residue, called endogenous residue. The mass of oxygen to be supplied for endogenous mass loss is proportional to the volatile mass that disappears from the system. This *net* behaviour is believed to be the outcome of a more complex set of mechanisms involving the growth of primary organisms (e.g. bacteria) and predators on these organisms (e.g. protozoa). Dold, Ekama and Marais (1980) proposed and formulated the net behaviour as a uniform organism mass having a death-

regeneration component, an approach which approximates the prey-predator system under certain circumstances.

Using the death-regeneration approach Dold *et al* (1980) in their development of the general activated sludge process model, and van Handel and Marais (1981) in their extension of this model to denitrification, have shown that the response of all the known process types (including nutrient removal processes) can be simulated very closely, even under cyclic flow and load conditions. Under constant flow and load, the death-regeneration approach reduces to the endogenous mass loss approach. This latter approach leads to relatively simple process equations (Marais and Ekama, 1976) and constitutes the basic design equations in this manuscript, see Eqs. (4.6 to 4.19).

3. PROCESS KINETICS

3.1 Mixing Régimes

In the activated sludge process, the mixing régime in the reactor and the sludge return influence the response of the process - consideration must be given to reactor kinetics.

There are two extremes of mixing; completely mixed and plug flow.

In the completely mixed régime the influent is instantaneously and thoroughly mixed (theoretically) with the reactor contents. Hence the effluent flow from the reactor has the same constitution as the reactor contents. The reactor effluent flow passes to a settling tank; the overflow from the tank is the stabilized waste stream, the underflow is concentrated mixed liquor and recycled back to the reactor.

In the completely mixed system the rate of return of the underflow has no effect on the reactor process except if an undue sludge build-up occurs in the settling tank. The shape of the reactor is approximately square or circular in plan, and mixing is usually by mechanical aerators but also can be effected by bubble aeration. Examples are extended aeration plants, aerated lagoons, Pasveer ditch and completely mixed activated sludge plants.

In a plug flow régime, the reactor usually is a long channel type basin. The influent is introduced at one end of the channel, flows along the channel axis and is mixed by air sparges set along one side of the channel. Theoretically each volume element of liquid along the axis is assumed to remain unmixed with the elements leading and following. Discharge to the settling tank takes place at the other end of the channel. To innoculate the influent waste flow with organisms, the underflow from the settling tank is returned to the influent end of the channel. This creates an intermediate flow régime, deviation from true plug flow conditions depending on the magnitude of the recycled underflow. Conventional activated sludge plants are of the intermediate flow régime type with recycle ratio varying from 0,25 to 3 times the influent flow rate. If the recycle rate is raised very high, the mixing régime approaches that of complete mixing.

Intermediate flow régimes are also achieved by having completely mixed reactors in series, or by step-aeration. In the latter, the influent is fed at a series of points along the axis of the plug flow type reactor. Both configurations require, for inoculation purposes, recycling of the sludge from the settler to the influent point.

The mean kinetic response of an activated sludge process, i.e. sludge mass, daily sludge production, daily oxygen demand and effluent quality is adequately, indeed accurately given by assuming the process is completely mixed and the influent flow and load are constant. This allows the plant volume, the mass of sludge wasted daily and mean daily oxygen demand to be determined by relatively simple formulations. Peak oxygen demands which arise under cyclic flow and load conditions can be estimated subsequently quite accurately by applying an adjustment to the mean daily demand, so also for other parameters. These adjustments have been developed from simulation studies, using the general model of Dold, Ekama and Marais (1980), on processes operated under cyclic and under constant flow and load conditions. For details see Chapter 6, Section 7.6.2.

3.2 Sludge Age

A diagrammatic sketch of the completed mixed process with sludge recycle is given in Fig. 4.1. This sketch differs from that usually presented in that the sludge wasted each day is abstracted directly from the reactor - the common practice is that the waste sludge is abstracted from the secondary settler underflow. Sludge abstraction directly from the reactor leads to a method of control of the sludge age, called the *hydraulic control of sludge age*, which has significant advantages compared to control by wastage via the underflow, see Section 10.

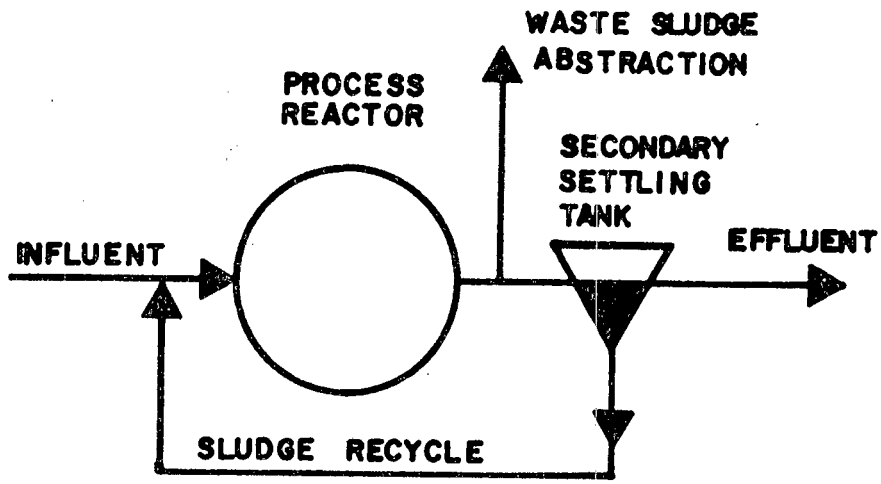


Fig. 4.1 *A diagrammatic representation of the completely mixed activated sludge process with hydraulic control of sludge age and sludge recycle.*

The sludge age, R_s, in days, is defined by:

$$R_s = \frac{\text{mass of sludge in reactor}}{\text{mass of sludge wasted per day}} \quad \text{(days)} \qquad (4.1)$$

By abstracting the sludge directly from the reactor, the wasted liquor and reactor liquor concentrations are the same. If a sludge age of, say, 10 days is required, one tenth of the *volume of the reactor* must be wasted every day.* This can be achieved by a constant draw-off at flow rate, q, per day where q.1 day = v, the volume to be wasted,

hence

$$R_s = \frac{XV_p}{Xv} = \frac{XV_p}{Xq} = \frac{V_p}{q} \qquad (4.2)$$

where

V_p = volume of the process reactor (ℓ)

3.3 Nominal Hydraulic Retention Time

In activated sludge theory the volume of the process per unit of volume of influent flow is known as the nominal process hydraulic retention time i.e.

$$R_{hn} = V_p/Q \qquad (4.3)$$

where

R_{hn} = average nominal process hydraulic retention time (d)

Q = daily average influent flow rate (ℓ/d)

3.4 Effluent COD Concentration

Under normal activated sludge process operating conditions in South Africa, where the sludge ages are in excess of 10 days (to ensure nitrification *and* nutrient removal) the nature of the influent COD in municipal wastewaters is such that the COD concentration in the effluent is inconsequential in the process design - the soluble readily

*This assumes that the mass of sludge in the secondary settling tanks is negligible with respect to that in the process reactors. This assumption is valid when the process is operated at high underflow recycle ratios

biodegradable COD fraction is completely utilized in a very short period of time (less than 1 hour) and the particulate COD, whether biodegradable or unbiodegradable, is adsorbed or enmeshed in the sludge flocs, and settles out with the sludge in the secondary settling tanks. Consequently, *the effluent COD concentration is comprised virtually wholly of the soluble unbiodegradable COD* (from the influent)plus the COD of the sludge particles which escape with the effluent due to imperfect operation of the secondary settling tank (see Chapter 3, Section 7). Hence the effluent COD concentration, S_{te}, is approximately given by

$$S_{te} = S_{us} \qquad (4.4a)$$

for filtered samples, or,

$$S_{te} = S_{us} + f_{cv}.X_{ve} \qquad (4.4b)$$

for unfiltered samples, where

S_{us} = unbiodegradable COD in the effluent

= $S_{usi} = f_{us}\ S_{ti}$ (mgCOD/ℓ) (see Eq 2.3)

X_{ve} = volatile solids concentration in the effluent (mgVSS/ℓ)

f_{cv} = COD/VSS ratio of the volatile solids

= 1,48 mgCOD/mgVSS.

4. PROCESS DESIGN EQUATIONS

Once it is recognized that all the COD in the influent, except the soluble unbiodegradable COD, is either utilized by the micro-organisms to form micro-organism mass, or remains in the process and accumulates as inert sludge mass, it follows that the mass of sludge produced and the carbonaceous oxygen demand in the process are functions of the mass of COD to be treated daily; the greater the daily COD mass load, the greater the sludge production and carbonaceous oxygen demand.

The equations* given below give the masses of sludge generated in

*The derivation of these equations is given by Marais and Ekama (1976) and a list of symbols used in the equations is given in Appendix 1.

the process and the oxygen demand for COD removal as a function of the total COD load, the wastewater characteristics i.e. the unbiodegradable soluble and particulate COD fraction (f_{us} and f_{up}) and the sludge age. The constants in the equations i.e. the specific yield coefficient Y_h, the specific endogenous mass loss rate b_h, the unbiodegradable fraction of the active mass f, and the COD/VSS ratio of the sludge f_{cv}, as well as their temperature dependencies are given in Table 4.1.

Table 4.1 Kinetic constants and their temperature dependency for the steady state carbonaceous degradation activated sludge model (ex Marais and Ekama, 1976)

Constant	Symbol	Temperature Dependency Equation	θ	Standard Value (20°C)	Eq. No.
Yield Coefficient (mg VSS/mg COD)	Y_h	remains constant	1,000	0,45	
Endogenous Respiration Rate	b_h	$b_{hT}=b_{h20}\theta^{(T-20)}$	1,029	0,24	(4.5)
Endogenous Residue (mg VSS/mg VSS)	f	remains constant	-	0,20	
COD/VSS Ratio (mg COD/mg VSS)	f_{cv}	remains constant	-	1,48	

In the equations below, the prefix M denotes the mass of the parameter which follows in brackets, i.e.

1. *Influent*

$$M(S_{ti}) = Q.S_{ti} \quad \text{mg COD/d} \quad (4.6)$$

$$M(S_{bi}) = Q.S_{bi} \quad \text{mg COD/d} \quad (4.7a)$$

$$= Q.S_{ti}\ (1 - f_{us} - f_{up}) \quad \text{mg COD/d} \quad (4.7b)$$

$$= M(S_{ti})\ (1 - f_{us} - f_{up}) \quad \text{mg COD/d} \quad (4.7c)$$

$$M(X_{ii}) = Q.X_{ii} \quad \text{mg VSS/d} \quad (4.8a)$$

$$= Q.f_{up}\ S_{ti}/f_{cv} \quad \text{mg VSS/d} \quad (4.8b)$$

$$= M(S_{ti})\ f_{up}/f_{cv} \quad \text{mg VSS/d} \quad (4.8c)$$

2. *Process*

$$M(X_a) = V_p X_a \quad \text{mg VSS} \tag{4.9a}$$

$$M(X_e) = V_p X_e \quad \text{mg VSS} \tag{4.9b}$$

$$M(X_i) = V_p X_i \quad \text{mg VSS} \tag{4.9c}$$

$$M(X_v) = V_p X_v \quad \text{mg VSS} \tag{4.9d}$$

$$M(O_c) = V_p O_c \quad \text{mg O/d} \tag{4.9e}$$

(a) The Active Volatile Solids Mass (mg VSS)

$$M(X_a) = M(S_{bi}) \, Y_h R_s \, / \, (1 + b_h R_s) \quad \text{(mg)}$$

$$= (1 - f_{us} - f_{up}) \, M(S_{ti}) \, Y_h R_s / \, (1 + b_h R_s) \tag{4.10}$$

(b) The Endogenous Residue Volatile Solids Mass (mg VSS)

$$M(X_e) = f \, b_h R_s \, M(X_a) \quad \text{(mg)} \tag{4.11}$$

(c) The Inert Volatile Solids Mass (mg VSS)

$$M(X_i) = M(X_{ii}) \, R_s \quad \text{(mg)}$$

$$= M(S_{ti}) \, (f_{up} / f_{cv}) R_s \tag{4.12}$$

(d) The Total Volatile Suspended Solids Mass (mg VSS)

$$M(X_v) = M(X_a) + M(X_e) + M(X_i)$$

$$= \frac{Y_h \, R_s \, M(S_{bi})}{(1 + b_h \, R_s)} \quad (1 + f \, b_h \, R_s) + M(X_{ii}) \, R_s \quad \text{(mg)}$$

$$= M(S_{ti}) \, R_s \left\{ \frac{(1 - f_{us} - f_{up}) \, Y_h}{(1 + b_h R_s)} \, (1 + f b_h R_s) + \frac{f_{up}}{f_{cv}} \right\} \tag{4.13}$$

(e) The Total Suspended Solids Mass (mg TSS)

$$M(X_t) = M(X_v)/f_i \tag{4.14}$$

where

f_i = MLVSS/MLSS ratio of the sludge.

6. The Carbonaceous Oxygen Demand (mg O/d)

$$M(O_c) = M(\text{O synthesis}) + M(\text{O endogenous mass loss})$$

$$= (1-f_{cv}Y_h)\, M(S_{bi}) + f_{cv}(1-f)\, \overline{b_h\, M(X_a)} \quad (\text{mg O/d})$$

$$= M(S_{ti})(1-f_{us}-f_{up})\, \{(1-f_{cv}Y_h)+f_{cv}(1-f)b_h \frac{Y_h R_s}{(1+b_h R_s)}\} \qquad (4.15)$$

Knowing the mass of mixed liquor (MX_t or MX_v) in the process, the volume of the process is determined from the value specified for the MLSS or MLVSS concentration, X_t, or X_v respectively,

$$V_p = M(X_t)/X_t = M(X_v)/X_v \qquad (4.16)$$

Knowing the volume V_p, the total nominal hydraulic retention time, R_{hn}, then is found from the specified daily average flow rate Q, using Eq (4.3).

The above design equations lead to the following important conclusions:

The mass of volatile solids in the reactor is a function only of the mass of COD utilized per day and the sludge age. Consequently, insofar as the mass of sludge is affected, it is immaterial whether the mass of COD utilized arises from a low daily flow with a high COD concentration, or a high daily flow with a low COD concentration; provided $M(S_{ti})$ is the same in both instances, the masses of sludge will be identical. However, the hydraulic retention times will differ, being long in the first and short in the second instance, respectively. The hydraulic retention time, therefore, is incidental to the COD mass utilized, the MLVSS and the daily flow - it serves no basic kinetic function in steady state operation.

The active volatile mass $M(X_a)$ in the process is the live organism mass which performs the biodegradation processes. The remaining volatile masses, $M(X_e)$ and $M(X_i)$ are inactive and do not serve any function insofar as the biodegradation mechanisms in the process are concerned. The active fraction of the sludge mass with respect to the volatile solids f_{av} is given by

$$f_{av} = M(X_a) \,/\, M(X_v) \tag{4.17}$$

substituting for $M(X_a)$ and $M(X_v)$ and noting that

$$M(S_{bi}) = (1 - f_{us} - f_{up})\, M(S_{ti}) \quad \text{and}$$

$$M(X_{ii}) = (f_{up}/f_{cv}).\, M(S_{ti}) \quad \text{yields}$$

$$\frac{1}{f_{av}} = 1 + fb_h R_s + \frac{f_{up}\,(1 + b_h\, R_s)}{f_{cv} Y_h (1 - f_{us} - f_{up})} \tag{4.18}$$

If the total suspended solids mass (TSS) is used as the basis for determining the active fraction, then the active fraction of the sludge mass with respect to the total suspended solids f_{at} is given by

$$f_{at} = f_i\, f_{av} \tag{4.19}$$

where

f_i = MLVSS/MLSS ratio of the sludge.

The design equations set out above form the starting point for all the activated sludge processes considered in this manuscript, from the relatively simple single reactor complelely mixed aerobic process, to the more complex multi-reactor anoxic-aerobic and the anaerobic-anoxic-aerobic processes. For these more complex systems the basic equations apply only if the constraints imposed on the processes are adhered to. Provided this is done the effects of nitrification and nitrification-denitrification and the associated oxygen demands can be formulated as additional to the basic equations. That this "simplified" approach is adequate for design has been established by the close correlation achieved when comparing the mean response of the process predicted by the general theory (and verified experimentally) with that predicted by the basic and additional equations.

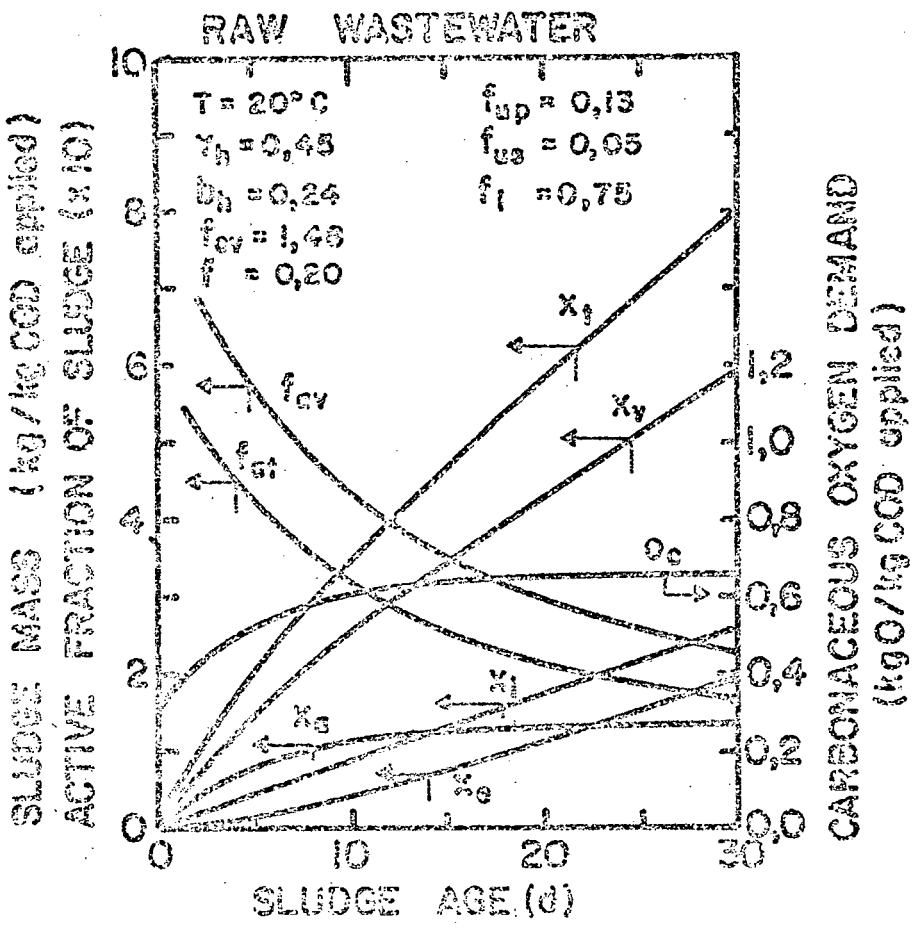
It is important to take cognizance of the constraints. For example, in anoxic-aerobic processes an upper limit is imposed on the fractional mass of sludge that may exist unaerated. If exceeded, then

inter alia the mass of sludge produced per day increases and the carbonaceous oxygen demand decreases below that predicted by the basic equations. The reason for these deviations lies in the kinetics of degradation of the slowly biodegradable particulate material - if the aerobic fraction of the sludge mass is too small the particulate material is only partially metabolized and accumulates in the process as additional volatile solids; concomitantly the carbonaceous oxygen demand is reduced. Evidently where such conditions apply the basic equations become inappropriate; however approximate solutions are sometimes obtainable by simulation using the general model, (see Arkley and Marais (1982) and Sehayek and Marais (1981) for a detailed discussion).

5. STEADY STATE DESIGN CHART

Plots of Eqs(4.10 to 4.15 and 4.18 to 4.19) are shown in Fig. 4.2 for a unit mass of $M(S_{ti})$. The values of the kinetic constants, Y_h, b_h, f_{cv} and f are those listed in Table 4.1 for 29°C and have been verified in extensive laboratory and pilot scale investigations (Ekama and Marais, 1978). The values of the unbiodegradable particulate and soluble COD fractions (f_{up} and f_{us} respectively) are listed in Table 4.2, for raw and settled municipal wastewaters.

The plots in effect give the masses $M(X_a)$, $M(X_e)$, $M(X_i)$, $M(X_v)$ and $M(X_t)$ contained in the reactor for a unit mass of COD applied per day for sludge ages up to 30 days. Also shown is the associated mass of oxygen to be supplied per day for carbonaceous material degradation and the active fraction of the sludge with respect to



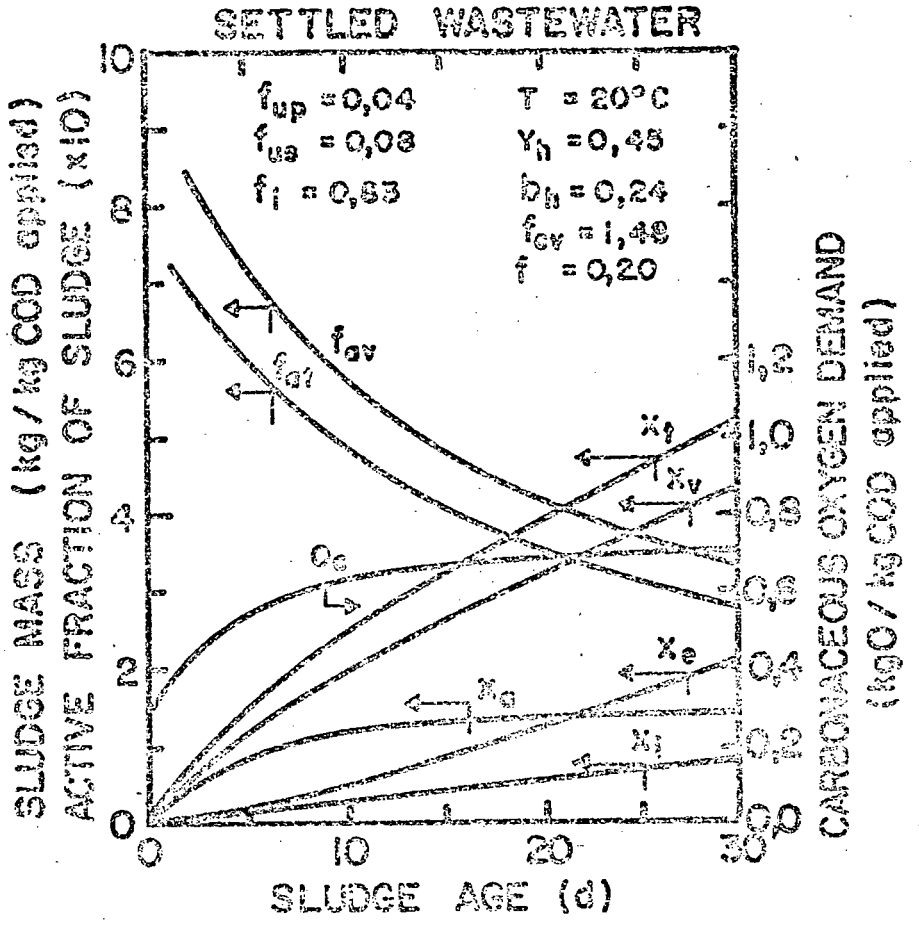


Fig 4.2 *Active (X_a), endogenous (X_e), inert (X_i), volatile (X_v), total (X_t), and carbonaceous oxygen demand (O_c) per kg COD applied to the biological process, and active fraction with respect to volatile solids (f_{av}) and total solids (f_{at}) versus sludge age for raw (Fig 4.2a, left) and settled (Fig 4.2b, right) wastewaters at 20°C*

Table 4.2 Influent wastewater fractions for settled and unsettled sewage

Sewage Fraction	Sewage	
	Unsettled	Settled
Soluble Unbiodegradable fraction, f_{us} (mg COD/mg COD)	0,05	0,08
Particulate Unbiodegradable fraction, f_{up} (mg COD/mg COD)	0,13	0,04
MLVSS/MLSS ratio (f_i)	0,75	0,83

VSS (X_v) and TSS (X_t). The volumes of the reactors at two different sludge ages will be in direct proportion to the masses $M(X_t)$ or $M(X_v)$ if the mixed liquor concentrations, X_t or X_v are specified to be the same in both plants.

The diagrams show that the active mass increases fairly rapidly with an increase in sludge age up to about 10 days sludge age, thereafter it increases only marginally. The carbonaceous oxygen demand shows a similar behaviour; at zero sludge age the oxygen demand is that due to synthesis, additional oxygen demand at sludge ages greater than zero is due to endogenous respiration which is proportional to the active mass. In contrast the fractions of endogenous and inert solids increase rapidly relative to the active mass at sludge ages greater than 10 days and consequently in processes treating raw wastewater at sludge ages longer than 10 days, only a small fraction of the sludge mass is active.

In design, the following sequence of calculation is suggested:

Select values for f_{up} and f_{us} which are believed to best represent these fractions of the wastewater. Select the MLVSS/MLSS ratio of the sludge produced. Determine:-

a) S_{upi} (Eq 3.4), S_{usi} (Eq 3.3), X_{ii} (Eq 3.6)

b) $M(S_{ti})$ and/or $M(S_{bi})$

c) $M(X_a)$(Eq 4.10), $M(X_e)$(Eq 4.11), $M(X_i)$(Eq 4.12), $M(X_v)$(Eq 4.13), $M(O_c)$(Eq 4.15) and $M(X_t)$(Eq 4.14)

d) V_p (Eq 4.16)

e) R_{hn} (Eq 4.3)

f) S_{te} (Eqs 4.4a or b)

In the design sequence set out above the input COD and its characteristics will be governed by the specific waste flow. The parameter that requires selection is the sludge age; this will depend on the objectives for the plant, for COD removal only, nitrification etc. Specification of the sludge, therefore, is an important design decision and requires special consideration, see Section 11. For our general purpose however, we will proceed to show how the various parameters such as reactor volume, oxygen demand, etc. are affected by the sludge age.

6. PROCESS VOLUME REQUIREMENTS

In Section 4 above a procedure is set out whereby the volume of the reactor is estimated. This involves determining the mass of sludge accumulated for a specified sludge age and a specified COD mass loading per day; the volume is then determined by diluting the mass of sludge accumulated to a specified mixed liquor concentration. Once the volume is fixed, the retention time, or aeration time, also is fixed (by Eq 4.3). Hence retention time, or aeration time, is immaterial in the design and it is merely a consequence of the kinetics governing the process. This point is mentioned specifically because some design procedures lay stress on the aeration time as a design parameter, a procedure that can result in serious miscalculation of the volume requirements. Compare, for example, two plants operating at the same sludge age, both receiving the same mass of COD per day but the first at high concentration and low flow and the second at a low concentration and high flow. If designed on a specified retention time, the volume of the first will be much smaller than that of the second whereas the sludge mass contained in the reactors will be identical. Consequently the first plant may have an inordinately high MLSS concentration which may cause problems in the secondary settling tank.

Retention time therefore is a completely inappropriate parameter for design and other purposes such as a criterion for comparing the tankage requirements of different plants.

To form an overall impression of the volume requirement and in order to make valid comparisons on the volume requirements between different plants, the volume per unit COD input is a much superior parameter. This method involves the specification of an MLVSS or MLSS concentration (X_v or X_t) from which the reactor volume is determined from the sludge mass produced per unit COD load at the required sludge age (see Fig 4.2). Furthermore, in order to assess the effects of primary sedimentation it is preferable to relate the volume requirements to the input COD to the treatment works, for example for settled wastewater, the COD load on the process is reduced i.e. $S_{ti(process)} = S_{ti(works)} (1-f_{rps})$ where f_{rps} = fraction of COD removed by primary sedimentation. It is $S_{ti(process)}$ which fixes the sludge mass and because for settled wastewater S_{ti} is up to about 40% less than for raw wastewater, the process volume for settled wastewater accordingly will be much lower than that for raw wastewater.

From Eqs (4.13, 4.14 and 4.16) the process volume requirements on the basis of process COD load is found by calculating the mass of sludge, $M(X_t)$, generated from the total influent COD load $M(S_{ti})$ and assuming an MLVSS/MLSS ratio for the sludge mass i.e.

$$V_p X_t f_i = Q.S_{ti} R_s \{ \frac{(1-f_{us}-f_{up})Y_h(1+fb_hR_s)}{(1+b_hR_s)} + \frac{f_{up}}{f_{cv}} \} \qquad (4.20)$$

and hence the process volume requirements per *unit* COD load to the works for a specified MLSS concentration X_t and assumed MLVSS/MLSS ratio f_i is given by

$$\frac{V_p}{Q.S_{ti}} = \frac{R_s}{X_t f_i} \{ \frac{(1-f_{us}-f_{up})Y_h(1+fb_hR_s)}{(1+b_hR_s)} + \frac{f_{up}}{f_{cv}} \} \qquad (4.21a)$$

Taking the wastewater characteristics for raw wastewater given in Table 4.2, and the values of the kinetic constants given in Table 4.1, a plot of process volume requirements in m^3/kg COD applied per day versus sludge age for different MLSS concentrations in kg/m^3 is given in Fig 4.3. Clearly, the lower the specified MLSS concentration and the longer the sludge age, the larger the process volume per unit COD load.

The process volume requirements may also be determined from the equivalent COD load per capita. The vertical axis on the right hand side of Fig 4.3 is scaled on the basis that the equivalent COD load per capita for raw wastewater is 0,10 kg COD/d. Hence treating raw wastewater at a sludge age of 25 days and an MLSS concentration of 5 kg/m^3, a process volume of 145 ℓ/capita is required or 1,45 m^3/kg COD applied per day.

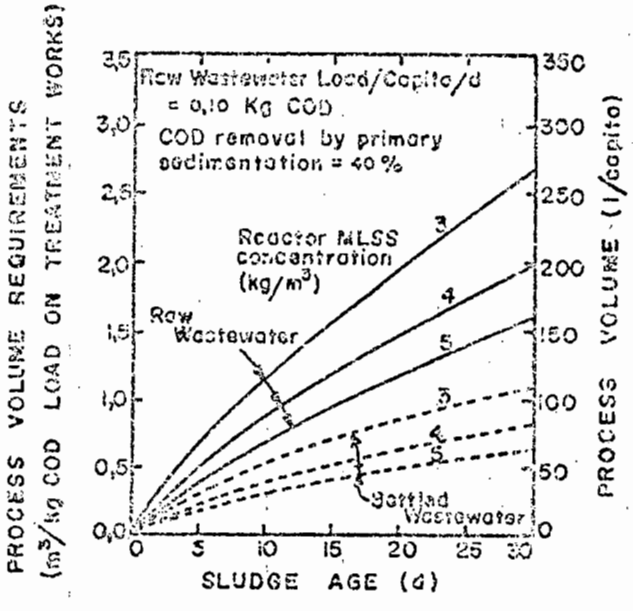


Fig 4.3 *Process volume requirements in m^3/kg COD raw wastewater load versus sludge age at different average process MLSS concentrations for raw and settled wastewater (assuming 40% COD removal by primary sedimentation). Process volume requirements in ℓ/capita also given based on a raw wastewater COD contribution of 0,10 kg COD/capita/d*

The comparative process volume requirements for settled wastewater per unit COD load on the treatment works also can be determined from Eq (4.21a), provided the COD fraction removed by primary sedimentation is incorporated in Eq (4.21a) by multiplying right hand side of Eq (4.21a) by $(1-f_{rps})$ and inserting the appropriate f_{up} and f_{us} values for settled wastewater i.e.

$$\frac{V_p}{S_{ti}Q} = \frac{R_s}{X_t f_i} \left\{ \frac{(1-f_{us}-f_{up})Y_h(1+fb_hR_s)}{(1+b_hR_s)} + \frac{f_{up}}{f_{cv}} \right\} (1-f_{rps}) \qquad (4.21b)$$

where S_{ti} = total COD concentration in treatment works.

The process volume requirements for settled wastewater are shown also in Fig 4.3 for the f_{up}, f_{us} and f_i values given in Table 4.2 assuming primary sedimentation removes 40% of the COD load (f_{rps} = 0,40). From Fig 4.3, treating settled wastewater at a sludge age of 25 days and an MLSS concentration of 5 kg/m³, a process volume of 0,60 m³/kg raw COD load to the works or 60ℓ/capita is required. Comparing the process volume treating raw or settled wastewaters it can be seen that a significant reduction in process volume can be obtained through primary sedimentation.

7. CARBONACEOUS OXYGEN DEMAND

The mean daily carbonaceous oxygen demand per unit COD discharged to the *process* is shown plotted versus sludge age at 20°C for raw and settled wastewater in Figs 4.2a and b respectively (calculated from Eq 4.15) - for treatment of raw wastewater S_{ti} = COD of the raw wastewater; for treatment of settled wastewater S_{ti} = (COD of raw wastewater)$(1-f_{rp})$. These diagrams show that for sludge ages longer than 15 days the increase in carbonaceous oxygen demand per unit process COD load $\{M(O_c)/M(S_{ti})\}$ is marginal with increase in sludge age for both raw and settled wastewater. The carbonaceous oxygen demand per unit process COD load for raw and settled wastewater is usually within 10% of each other, with the demand for settled wastewater being the higher value. This is because compared to raw

wastewater, more of the total COD in settled wastewater is biodegradable, i.e. $(1-f_{us}-f_{up})$ usually is greater for settled wastewater than for raw wastewater (see Eq 3.7) but the difference is small. This can be seen in Figs 4.2a and b - at 20 days sludge age, the carbonaceous oxygen demand per unit COD load is 0,635 kgO/kgCOD for raw wastewater and 0,682 kgO/kgCOD for settled wastewater. Although there is only a small difference in carbonaceous oxygen demand *per unit process COD load* between raw and settled wastewaters there is a substantial difference in the O_2 demand per unit COD load *to the works*. For settled wastewater, this is given by 0,682 $(1-f_{rps})$ which for f_{rps} = 0,40 gives 0,41 kgO/kgCOD load on the works. Clearly primary sedimentation will lead to significant aeration energy savings - because primary settling tanks remove about 30 to 40% of the raw influent COD, the carbonaceous oxygen demand for settled wastewater will be about 30 to 40% lower than that for raw wastewater.

The carbonaceous oxygen demand is the oxygen demand for the oxidation of the influent COD only. In nutrient removal processes oxygen is also required for nitrification i.e. the oxidation of ammonia to nitrate, and some oxygen is recovered during denitrification i.e. reduction of nitrate to nitrogen gas. The total oxygen demand for a nutrient removal process therefore is given by the sum of the carbonaceous and nitrification demands less that recovered by denitrification. The procedures for calculating the oxygen demand for nitrification and the oxygen recovered by denitrification are discussed in Chapters 5 and 6 respectively.

Owing to the daily cyclic nature of the COD load the carbonaceous oxygen demand will vary concomitantly. The TKN load will also very daily cyclically; in nitrification-denitrification plants the oxygen demand for nitrification and oxygen recovery with denitrification conjointly with the carbonaceous demand give rise to a net cyclic total demand. From simulations using the general model of Dold *et al* empirical rules for estimating the daily peak and trough net oxygen demands have been developed and are discussed in Chapter 6, Section 7.6.2.

8. DAILY SLUDGE PRODUCTION

The mass of sludge produced per day by the activated sludge process is equal to the mass of sludge wasted per day and is called waste activated sludge or secondary sludge. From the definition of sludge age (see Eq 4.1), the mass of sludge produced per day $M(\Delta X_t)$ is given by the mass of sludge in the process $\{M(X_t)\}$ divided by the sludge age (R_s) i.e.

$$M(\Delta X_t) = M(X_t)/R_s \qquad \text{mg TSS/d}$$

Substituting Eq (4.14) for $M(X_t)$ and simplifying, yields the sludge produced per day per mg COD load on the biological process i.e.

$$\frac{M(\Delta X_t)}{M(S_{ti})} = \frac{1}{f_i}\left\{\frac{(1-f_{up}-f_{us})Y_h}{(1+b_hR_s)}(1+fb_hR_s) + \frac{f_{up}}{f_{cv}}\right\} \qquad (4.22)$$

A plot of the daily total sludge mass (TSS) produced per unit COD load on the biological process (Eq 4.22) versus sludge age (R_s) is shown in Fig 4.4 for raw and settled wastewater (see Table 4.2 for wastewater characteristics). From Fig 4.4, it can be seen that the mass of sludge produced in the activated sludge process (per unit COD load on the biological process) decreases as the sludge age increases for both raw and settled wastewater but the rate of decrease is negligible at sludge ages longer than 20 days. Treating settled wastewater results in lower secondary sludge production per unit COD load on the biological process than treating raw wastewater. This is because the unbiodegradable particulate COD fraction (f_{up}) in settled wastewater is lower than that in raw wastewater. Temperature effects on secondary sludge production

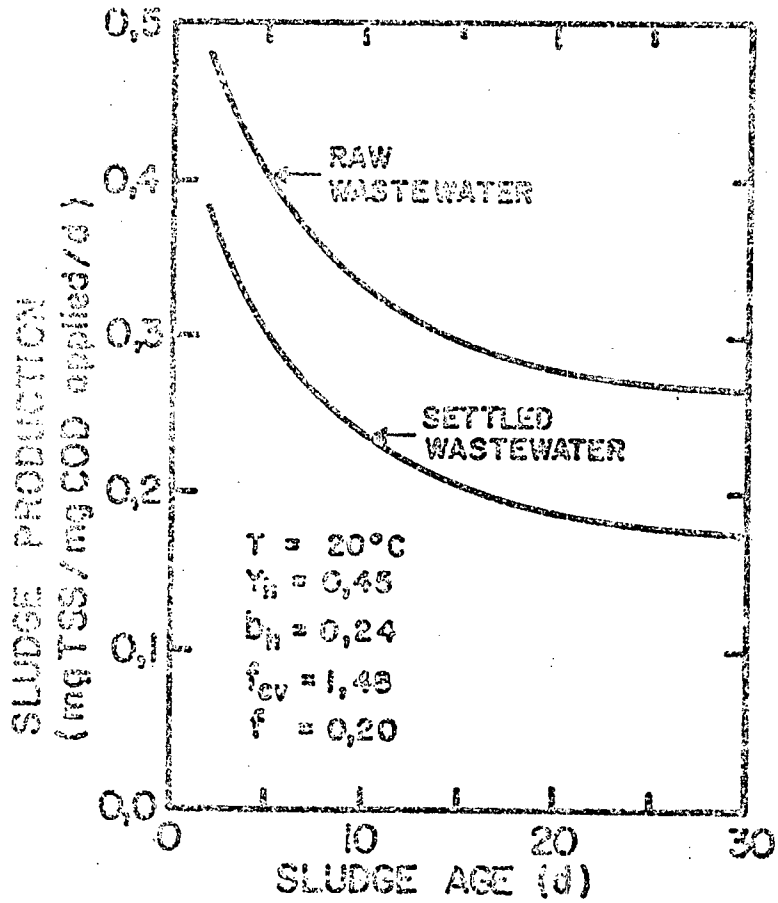


Fig 4.4 *Daily total suspended solids (TSS) sludge production in the activated sludge process (secondary sludge) per unit COD load on the process versus sludge age for raw (f_{up} = 0,13, f_{us} = 0,05 and f_i = 0,75) and settled (f_{up} = 0,04, f_{us} = 0,08 and f_i = 0,83) wastewaters at 20°C*

are small - sludge production at 14°C* is about 5% greater than at 20°C, a difference which is completely masked by the uncertainty in the estimates of the wastewater characteristics f_{up} and f_{us} and the MLVSS/MLSS ratio (f_i) of the sludge.

Although the sludge production of a plant treating settled wastewater is lower than that of a plant treating raw wastewater, the *total* sludge mass of sludge to be disposed of for a plant treating settled wastewater is higher because the total sludge includes both primary and secondary sludge - in plants treating raw

* Sludge production at 14°C can be calculated by adjusting b_h for temperature using Eq (4.5) in Table 4.1

wastewater, only secondary sludge is generated. The *total* sludge produced treating settled wastewater is slightly higher (by 10 to 20%) than that treating raw wastewater - this is because some of the settleable solids are biodegradable and are oxidized in the activated sludge process.

The daily production of secondary and primary sludges (when primary settling tanks are included in the treatment works) is the mass of sludge that needs to be disposed of by sludge handling methods. Sludge handling and disposal is not dealt with in this manual but the design of nutrient removal activated sludge processes should not be seen as separate from the design of the sludge disposal unit processes, in fact all unit processes of the treatment works from raw water pumping to ultimate disposal of sludge, should be viewed as an integrated system where the design of one unit process depends on the unit processes before it, and decisions on its design may affect the design of unit processes following it. The following examples will illustrate this - (1) in sludge handling practice there is evidence that a mixture of primary and secondary sludges thickens and dewaters better than secondary sludge alone; however in biological nutrient removal practice it has been found that when treating raw wastewater better removals of nitrogen and phosphorus are obtained than when treating settled wastewater - ease of sludge thickening and dewatering therefore need to be weighed against the higher nutrient removal, (2) when phosphorus rich waste biological sludges are subjected to anaerobic conditions, the phosphorus is released from the solid phase to the liquid phase; consequently, *supernatant* from waste sludge gravity thickeners may be phosphate rich and should not be discharged to the activated sludge process - in design, consideration should be given to chemically treating the gravity thickener supernatant to precipitate the phosphorus or, thickening the sludge by dissolved air flotation to prevent phosphorus release; (3) to improve biological excess P removal, the Johannesburg Municipality specifically operates one of the anaerobic digestors in an acid condition for the production of short chain organic compounds which are then discharged to the anaerobic reactor of the activated sludge process (see Chapter 3, Section 3,3) - consideration must be given at the design stage to the desirability of providing a specially designed facility for this purpose.

9. NUTRIENT REQUIREMENTS FOR SLUDGE PRODUCTION

All live biological material and many inert organic materials contain nitrogen and phosphorus. In the volatile suspended solids in the activated sludge process, the nitrogen content (as N with respect to VSS, f_n) ranges between 9% and 12% with an average of about 10%, and the phosphorus content (as P with respect to VSS, f_p), under purely aerobic conditions, ranges between 1% and 3% with an average of about 2,5%.

Under daily average conditions, the mass of nitrogen incorporated into the sludge mass is equal to the nitrogen content of the daily waste sludge. Accepting that the nitrogen content of the active, endogenous and inert volatile fractions are equal (which in most instances is a reasonable assumption), and equating the *concentration* of nitrogen required for daily sludge production per litre influent, N_s, to the nitrogen content of the waste sludge yields

$$Q.N_s = f_n \, M(X_v)/R_s$$

Substituting for $M(X_v)$ from Eq (4.10) and solving for the nitrogen requirements per unit COD, N_s/S_{ti} yields

$$\frac{N_s}{S_{ti}} = f_n \left[\frac{Y_h(1 - f_{us} - f_{up})}{(1 + b_h R_s)} \, (1 + fb_h R_s) + \frac{f_{up}}{f_{cv}}\right] \qquad (4.23)$$

where

f_n = nitrogen content of the volatile solids

= 0,10 mg N/mg VSS

To estimate the P requirement for daily sludge production, it is not correct to assume that the P content of the active, endogenous and inert volatile fractions is the same. The P content of the endogenous and inert volatile fractions (f_p) remain approximately constant at 1,5% whereas the P content of the active mass (γ) can vary from 3% to as

high as 35% depending on the different conditions in the process. Indeed, it is the propensity of the active mass to accumulate large quantities of P that is exploited in biological P removal processes. Accepting the different P contents of the active fraction and the endogenous and inert fractions, the concentration of P per ℓ influent (P_s) required for daily sludge production per mg/ℓ COD load (S_{ti}) is given by

$$\frac{P_s}{S_{ti}} = \left\{ \frac{(1-f_{up}-f_{us})Y_h}{(1+b_h R_s)} (\gamma + f_p f b_h R_s) + f_p \frac{f_{up}}{f_{cv}} \right\} \qquad (4.24)$$

where

γ = P content of the active mass (mg P/mg VSS)

f_p = P content of the inert and endogenous mass (mg P/mg VSS) = 0,015

The P incorporated into the sludge mass per unit COD (P_s/S_{ti}) is also the P removal from the wastewater per unit COD, $\Delta P/S_{ti}$. In the activated sludge process, under purely aerobic conditions the γ coefficient is about 0,03 mg P/mg VASS; when an anoxic reactor is included in the process, the coefficient is increased to about 0,06 mg P/mg VSS; when an anaerobic reactor is incorporated in the process, then, depending, amongst others, on the readily biodegradable COD concentration in the anaerobic reactor, the γ coefficient can vary between 0,06 to 0,35 mgP/mgVSS (see Chapter 7, Section 3.3). By stimulating high γ coefficients, with the aid of the anaerobic reactor, high P removals may be effected. This is the basis of biological P removal and is discussed in detail in Chapter 7.

A plot of Eqs (4.23 and 4.24) is given in Fig 4.5 for f_n = 0,10 mg N/mg VSS, γ = 0,03 mg P/mg VSS, f_p = 0,015 mg P/mg VSS, Y_h = 0,45 mg VSS/mg COD, b_h = 0,24/d at 20°C, P = 1,48 mg COD/mg VSS, and f = 0,20, versus sludge age (R_s) for raw (f_{us} = 0,05 and f_{up} = 0,13) and settled (f_{us} = 0,08 and f_{up} = 0,04) wastewaters.

From Fig 4.5, it is evident that greater quantities of nitrogen and phosphorus are required for sludge production from raw than from settled wastewaters. This is because greater quantities of sludge are produced per mgCOD process load when treating raw wastewaters. Furthermore, the nutrient requirements decrease as the sludge age increases because nett sludge production decreases as sludge age increases. Generally, for sludge ages greater than 10 days, the nitrogen removal attributable to nett sludge production is less than 0,025 mgN/mgCOD applied. As the influent TKN/COD ratio for domestic wastewater is in the approximate range 0,07 to 0,12, only a minor fraction of the influent nitrogen is

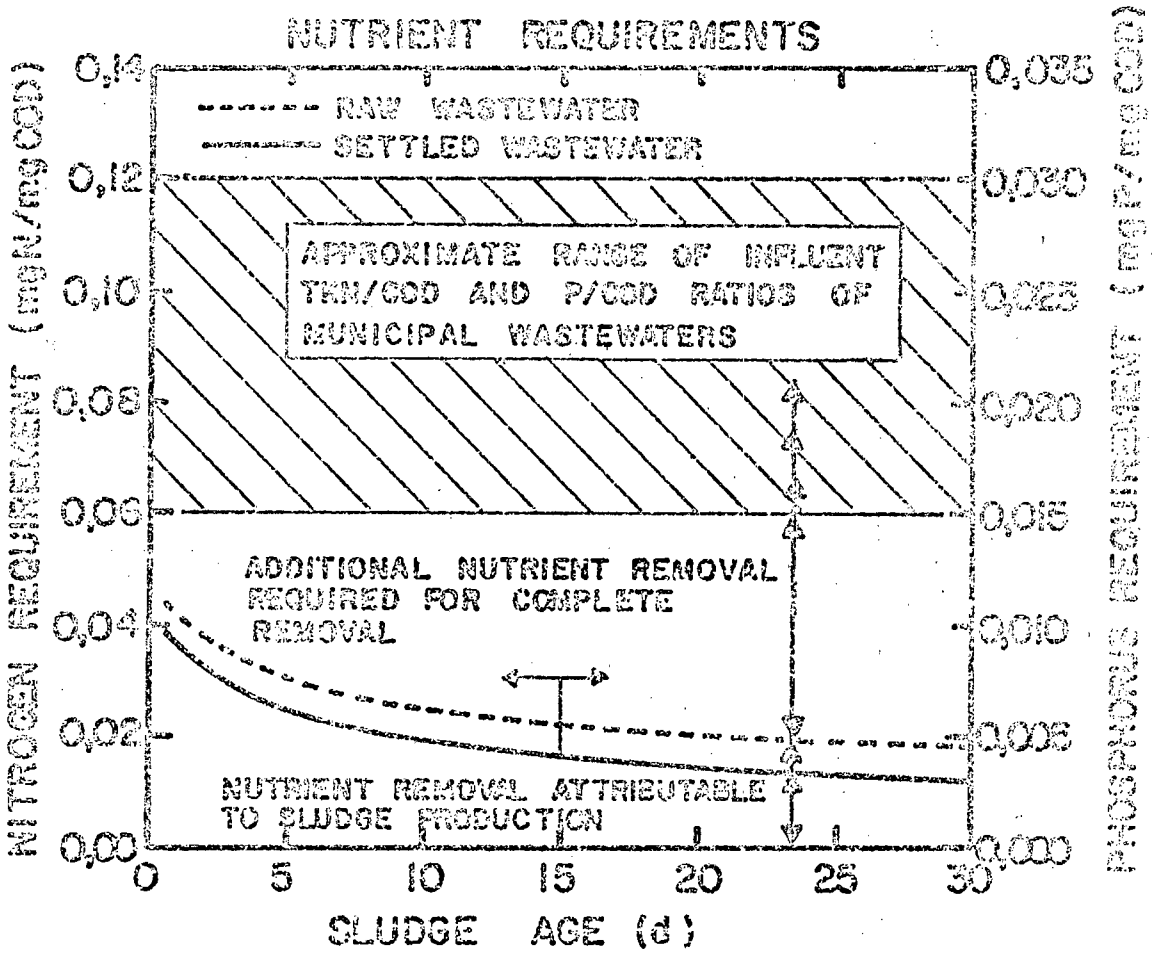


Fig 4.5 *Normal nutrient nitrogen and phosphorus requirements per kgCOD load in the activated sludge process versus sludge age together with influent nutrient loads per kgCOD.*

removed by sludge wastage; additional nitrogen removal is obtained only by nitrification and denitrification, the kinetics of which are discussed in Chapters 5 and 6. With regard to P removal, as the total P/COD ratio of domestic wastewaters usually ranges between 0,015 to 0,030, only a minor fraction of phosphorus, 0,005 mgP/mgVSS, can be removed by the aerobic activated sludge process; excess biological P removal is obtained by stimulating high γ coefficients in processes by incorporating an anaerobic reactor. Details of excess biological P removal are considered in Chapter 7.

10. PROCESS DESIGN AND CONTROL

The parameter of fundamental importance in the design and control of the activated sludge process is the sludge age. It is instructive to consider how this parameter influences both the control and design of the process and to contrast it to other design and control parameters that have been implemented in the past.

10.1 Sludge Age versus Load Factor as Control Parameter

A widely accepted basis for design (especially in North America and Europe) is the Load Factor (LF). It is also known as the Sludge Loading Rate (SLR) and has been used principally when the BOD_5 forms influent energy measurement parameter. The objective of the load factor was to form an estimate of the Food/Microorganism (F/M) ratio and as a result the load factor was defined as

$$LF = \frac{\text{mass of BOD load/d}}{\text{mass of sludge in process}}$$

$$= \frac{M(S_{BOD})}{M(X_v) \text{ or } M(X_t)} \qquad (4.25)$$

where

$M(S_{BOD})$ = mass of BOD load per day (mg)

$M(X_v)$, $(M(X_t)$ = mass of volatile (mgVSS) or total (mgTSS) suspended solids in process respectively.

A difficulty with the approach is that both the $M(X_v)$ and $M(X_t)$ measurements include unbiodegradable and inert material. To represent the F/M

ratio correctly, the LF should be defined as follows:

$$LF = F/M = M(\Delta S_{BOD})/M(X_a) \qquad (4.26)$$

where

$M(\Delta S_{BOD})$ = mass change in BOD across plant per day (mgBOD/d)

$M(X_a)$ = active mass in process (mgVASS)

As a practical control parameter, the F/M ratio as defined by Eq (4.26) is virtually unusable principally because $M(X_a)$ cannot be measured directly. It is for this reason that the LF was *approximated* by Eq (4.25)* with $M(X_v)$ or $M(X_t)$ as the solids parameter. In this form, however, the LF is an uncertain parameter against which to correlate the response of the process because $M(X_v)$ depends on both the biodegradable COD and the inert particulate material in the influent. For example, for the same biodegradable COD concentration, the LF will differ between settled and raw wastewaters whereas the oxygen demand and $M(X_a)$ will be the same for both. Furthermore the LF will be different depending on whether the settleable solids are measured in terms of MLVSS or MLSS. When the COD forms the influent energy measurement parameter, the LF is defined by Eq 4.27 which is even further out of place because the COD measure includes the unbiodegradable soluble and particulate COD fractions

$$LF = \frac{M(S_{COD})}{M(X_v) \text{ or } M(X_t)} \qquad (4.27)$$

where

$M(S_{COD})$ = mass of COD load per day.

If Eq (4.27) is written in terms of the mass change of COD per day across the plant (i.e. $M(\Delta S_{COD})$), then account of only the soluble unbiodegradable COD is taken. The unbiodegradable particulate COD affects the LF by increasing both the $M(\Delta S_{COD})$ and $M(X_v)$ or $M(X_t)$ so

*Because the effluent BOD usually is very small with respect to the influent BOD, the change in BOD mass load per day $M(\Delta S_{BOD})$ is closely approximated by the BOD mass load per day $M(S_{BOD})$.

that different load factors can be obtained depending on the unbiodegradable particulate COD fraction.

To overcome the problem of the unbiodegradable COD fractions on the LF, Marais and Ekama (1976) defined the F/M ratio in terms of COD as the mass change of biodegradable COD per day per unit *active* volatile mass and, to distinguish this parameter from the LF, called it the Substrate Utilization Rate with respect to the active mass, SUR_a i.e.

$$SUR_a = F/M = M(\Delta S_{COD})/M(X_a) \qquad (4.28)$$

where

$M(\Delta S_{COD})$ = mass change in biodegradable COD per day.

Again the SUR_a parameter is of little practical value because neither the $M(\Delta S_b)$ (due to the unknown unbiodegradable particulate COD content of the wastewater) nor the $M(X_a)$ can be measured. However, using Eq (4.28) as a basis, Marais and Ekama (1976) showed that the Substrate Utilization Rates with respect to the active mass (SUR_a), volatile mass (SUR_v) and total mass (SUR_t) can all be written in terms of sludge age, but different SUR's are obtained for a fixed sludge age depending on the parameters for measuring the sludge concentration (X_a, X_v or X_t) and the influent energy (COD or BOD) (see Fig 4.6).* Similarly for the same sludge age, different values of the LF or SLR can be obtained depending on the measurement parameters for the sludge concentration and influent energy.

The dependency of the SUR's, LF's or SLR's on the measurement parameters for the sludge concentration and influent energy is undesirable because it provides a permanent source of error and misunderstanding at, and between all levels of technical staff concerned with the process. But

*The derivation of some of these SUR values is given by Marais and Ekama and those for well settled wastewater (i.e. f_{up} = 0,00) are shown in Fig 4.6. It should be noted that if volatile inert material is present in the influent i.e. f_{up} > 0,00, e.g. in partially settled and raw wastewaters, a set of SUR values can be calculated for each selected value of f_{up}.

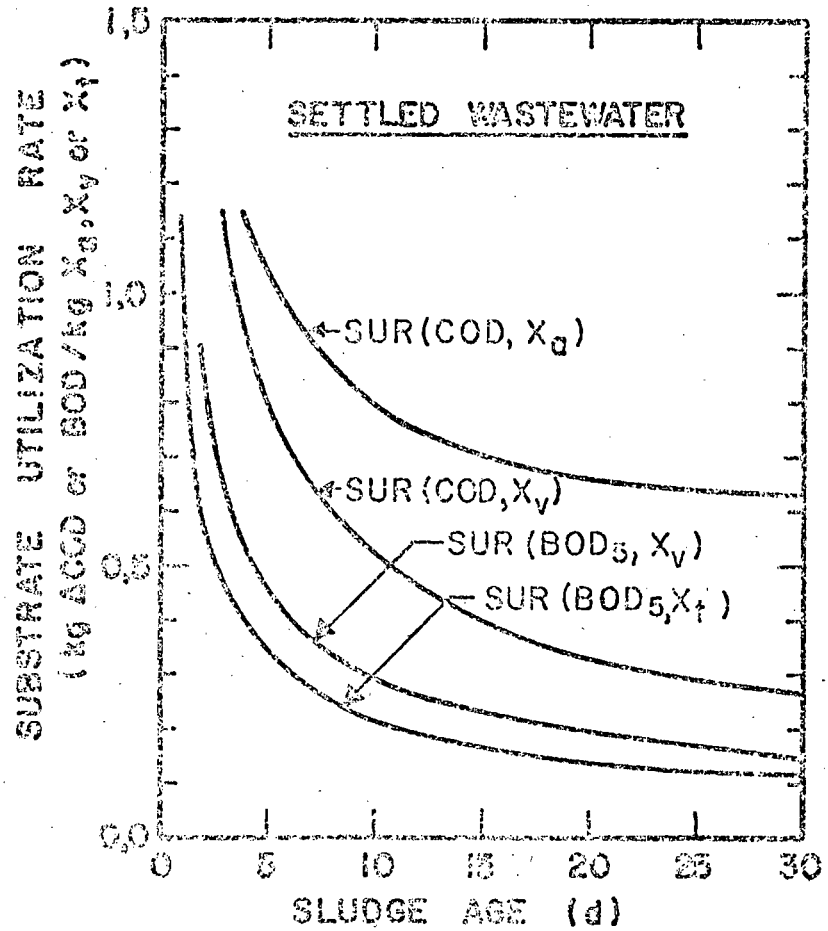


Fig 4.6 *Comparison between various substrate utilization rates (SUR) and sludge age.*

perhaps of greater importance is the fact *that all the different SUR's, LF's or SLR's are functionally related to the sludge age - no additional information can be derived from the SUR's, LF's or SLR's that cannot be derived from the sludge age.*

The sludge age therefore can replace completely the LF, SLR and SUR as a reference parameter. Furthermore, the sludge age can be fixed by a simple process control procedure if the process is appropriately designed. This control procedure is much more practical than procedures based on the LF approach.

10.2 Process Control

The usual control procedure of the activated sludge process involves keeping the sludge concentration at some value either specified from design considerations or established from experience

on the plant behaviour. Knowing the sludge concentration (X_v or X_t), to check that the LF is within the desired limits requires extensive testing over the day of the influent COD (or BOD) concentration and flow pattern to determine the daily COD (or BOD) *mass* load. To calculate the corresponding sludge age, a history of the daily sludge mass wastage needs to be kept. Often in conventional plants, the waste sludge is abstracted from the secondary settling tank underflow to benefit from the thickening function of the secondary settlers. However the sludge concentration of the underflow varies considerably with the daily cyclic flow through the plant (see Figs 4.7 and 4.8). Hence, each time sludge is wasted it is necessary to measure the underflow concentration and calculate the sludge age.

From the above, it is clear that in order to know the sludge age or the LF accurately, intensive testing of the plant and influent is required. This is manageable on large plants where the technical supervision is adequate, but on small plants both the Load Factor and sludge age usually are unknown.

The discussion above demonstrates that wasting sludge from the secondary settler underflow does not result in a simple and accurate control of either the sludge age or the LF. However, by using a different sludge wasting procedure, an accurate and simple control of the sludge age is possible. This different sludge wastage procedure is called the hydraulic control of the sludge age.

10.3 Hydraulic Control of Sludge Age

Hydraulic control of sludge age was first proposed and implemented in a generalized form by Garrett in 1958, based on a method of "modified sewage aeration" implemented by Setter, Carpenter and Winslow (1945).* It operates as follows: Suppose a sludge age of 10 days is specified. A satellite settling tank or dissolved air flotation unit is provided, completely independent of the secondary settling tank, to which 1/10 of the reactor volume is pumped every day. The supernatant is dis-

*For a review of the development of hydraulic control of sludge age see Ekama and Marais (1978).

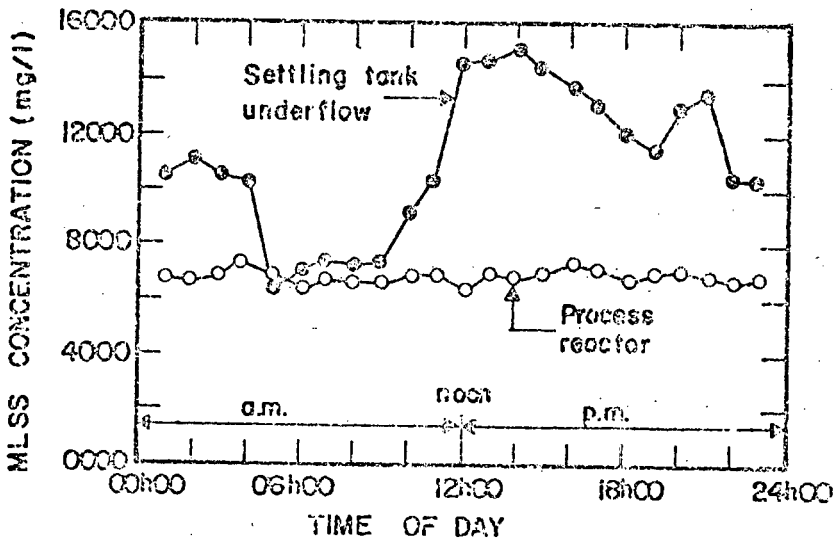
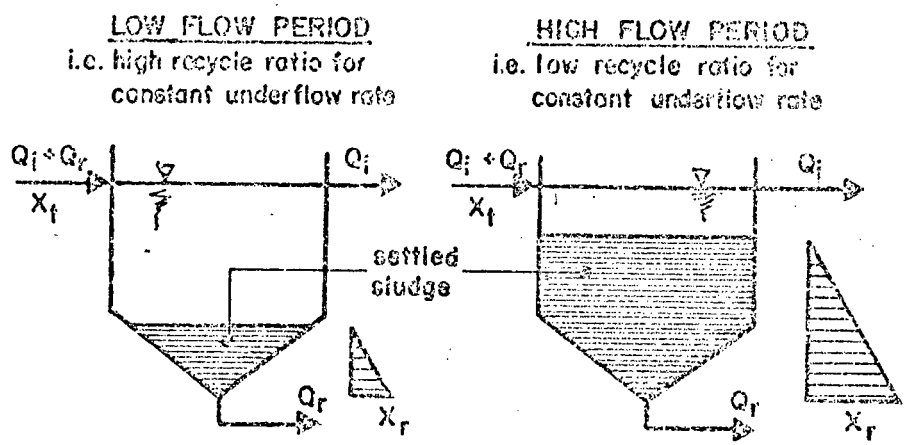


Fig 4.7 *Experimental data from a full scale activated sludge plant illustrating stability of the reactor MLSS concentration compared with that in the secondary settler underflow.*



Q_i = INFLUENT FLOW RATE (m^3/d)

Q_r = UNDERFLOW RATE (m^3/d)

X_f = SLUDGE DENSITY IN REACTOR (mg MLSS/l)

X_r = SLUDGE DENSITY IN UNDERFLOW (mg MLSS/l)

$$X_r = \frac{(Q_i + Q_r)}{Q_r} \cdot X_f = \frac{s+1}{s} \cdot X_f$$

$s = Q_r / Q_i$ = UNDERFLOW RECYCLE RATIO

Fig 4.8 *Increased sludge accumulation and higher underflow sludge concentration for (i) decreased recycle flow for fixed influent flow and (ii) increased influent flow for fixed recycle flow.*

charged to the effluent channel (or pumped back to the reactor),* the thickened sludge is pumped to the digestors or drying beds. That this method gives the correct sludge age can be seen from Eq (4.2) and the procedure works because the mixed liquor concentration changes insignificantly over the day. This is verified by comparing the stability of the concentration of mixed liquor in the reactor and the concentration of sludge in the underflow over the day in one of the major plants of Johannesburg, Fig 4.7, (Nicholls, 1975).

Controlling the sludge age in small works may require pumping at regular times, every day or every few days, provided the volume pumped is such that the required volume, v, per day is abstracted. On large plants the satellite settling tank (or flotation unit) may be designed for continuous operation receiving a constant flow, or, operated over a part of the day.

An important point about hydraulic control of the sludge age is that *irrespective of the flow through the plant* if a fixed fraction of the volume of the reactor is removed and wasted every day, the sludge age is fixed. If the COD mass load per day on the plant remains constant, the sludge concentration will remain constant automatically. If the COD mass load increases, the sludge concentration will increase automatically, to maintain the same sludge age. Thus, by monitoring the MLSS concentration and its changes for a fixed sludge age an indirect measure is obtained of the COD load and load change.

By means of the hydraulic control procedure, the sludge age may be changed by simply changing the volume wasted per day. If say, the sludge age is reduced from 25 days to 20 days by hydraulic control, the full effect of the change will become apparent only after about 15 days. Thus the organisms have an opportunity to adapt gradually to the change in load.

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*It should be noted that in a gravity thickener for waste sludge from a nutrient removal plant, considerable concentrations of phosphorus may be released in the thickener, which, when discharged to the activated sludge process will be counter productive for excess biological P removal. The thickener supernatant may have to be treated chemically to precipitate the P before discharge to the activated sludge process (see Section 8 above).

Hydraulic control of sludge age is particularly relevant to plants with sludge ages longer than about 4 days because for these plants the mass of sludge contained in the secondary settling tanks is a minor fraction of the total mass of sludge in the system. At sludge ages shorter than 4 days the mass of sludge in the secondary settling tanks becomes appreciable with respect to the total mass of sludge in the system. Hydraulic control will have to take cognizance of this and accuracy of the control will require additional testing. It should be noted that irrespective of the sludge age of the plant, the satellite settling tank required for hydraulic control will always be very small with respect to the secondary settling tanks - at 2 days sludge age the retention time is usually about 4 to 6 hours and hence the satellite settling tank has to accommodate 1/12th to 1/8th of the daily average flow; at 25 days sludge age the retention time is about $\frac{3}{4}$ to $1\frac{1}{4}$ days and the satellite settling tank has to accommodate about 1/20th of the daily average flow; in contrast the secondary settling tank has to accommodate 2 to 4 times the daily average flow.

With regard to design, hydraulic control of the sludge age has the following implications: It devolves a greater onus on the designer and removes responsibility from the plant operator: It becomes essential that the designer calculates the sludge mass more exactly, to provide sufficient reactor volume under the design load to allow for the required concentration of MLSS in the reactor at the specified sludge age. Also, the settling tank design, recycle and aeration capacities must be adequate. If these aspects are catered for adequately, then with hydraulic control of the sludge age, plant control is simplified and, on small scale plants, may even do away with the requirements for solids and SVI tests except at long intervals. Hydraulic control of sludge age makes the Sludge Loading Rate, SLR, (or Substrate Utilization Rate, SUR), redundant and introduces an entirely different attitude to process control.

11. SELECTION OF SLUDGE AGE

Selection of the sludge age is the most fundamental and important decision in the design of an activated sludge process. The sludge age of a plant depends on many factors *inter alia*, stability of the process, sludge settleability, whether or not the waste sludge should be suitable for direct discharge to drying beds, and most important of all the quality of effluent required i.e. is COD removal only acceptable, must the effluent be nitrified, is nitrogen and phosphorus removal required. Although the discussion below will be aimed at South African conditions, where nitrification is obligatory and stringent standards for the effluent phosphate concentration have been promulgated, other situations will be discussed briefly so as to place South African activated sludge process technology in perspective with other technologies, for example those of Europe and North America.

11.1 Short Sludge Ages (1-5 days)

Conventional plants: These plants are operated in the conventional configuration i.e. a semi plug flow configuration but modified systems such as contact stabilization, step aeration, step feed and others are also implemented.

Short sludge age plants are extensively used in Europe and North America but are virtually unknown in South Africa principally because the promulgated standards for effluents cannot be satisfied, i.e. that of obligatory nitrification.

Short sludge age plants are for the purpose of COD removal only, towards this objective sludge ages of 1 to 3 days are sufficient. BOD or COD reductions, for the conventional system range from 75 to 90%; the actual removal achieved depends on the influent, the state of the sludge and the efficiency of the settling tanks. Predatory activity of the micro-organisms in the sludge is relatively low which causes turbidity and high effluent COD.

Nitrification should be absent,or the plant can be operated to prevent nitrification; this however may be difficult to achieve with high water temperatures in the tropics.

Advantages with low sludge age plants are: small process volumes for unit input COD (Fig 4.3) with corresponding low carbonaceous oxygen demand (see Fig 4.2); nitrification is unlikely,giving a saving in the nitrification oxygen demand (see Fig 6.1); oxygen demand under cyclic flow and load tends to be heavily damped making control of the oxygen easier than with longer sludge age plants. Disadvantages are: the mass of sludge produced by unit COD input is high (Fig 4.4) and the active fraction of the sludge is high (Fig 4.2). The sludge treatment facilities accordingly constitute an appreciable fraction of the treatment costs although the running costs can be reduced by energy recovery from anaerobic digestion of the sludge (see below); the process tends to be unstable and sensitive to mechanical breakdown.

Because of the relatively low oxygen demand and the high sludge production per unit input COD it is possible to make these high rate processes near self sufficient with respect to energy requirements - sufficient methane gas can be produced by anaerobic digestion of the waste sludge to generate electricity for oxygen supply and process operation.

Aerated lagoons: In aerated lagoons, (as opposed to aerated oxidation ponds which supplement the oxygenation by algae) the oxygen requirement in the process is supplied wholly by aerators, usually floating mechanical ones. There are essentially two types of aerated lagoons, suspension mixed and facultative.

Suspension mixed aerated lagoons have sufficient energy input per unit volume by the aeration equipment to keep the sludge in suspension. In facultative lagoons this energy input is insufficient and settlement takes place on the lagoon floor, to form a sludge layer which decomposes anaerobically, as in an oxidation pond.

Kinetically, suspension mixed lagoons are members of the activated sludge process, the difference is only in that the former is a flow through system i.e. the sludge age equals the nominal hydraulic retention time,whereas the latter has a sludge recycle from the settling tank making the sludge age longer than the hydraulic retention time. Accordingly the volume of the aerated lagoon per unit input COD is large whereas it is small for the conventional short sludge plant. (For a sludge age of,say,1 day the aerated lagoon will have an hydraulic retention time of one day whereas the short sludge age conventional plant (with a one day sludge age) will have a hydraulic retention time of about 1/8th of a day.

The effluent from a suspension mixed aerated lagoon has the same constitution as the mixed liquor in the basin. The COD removed from the system via the oxygen demand is relatively small so that the COD in the effluent is quite unacceptable for discharge to receiving waters. In fact the principal objective of all short age plants is to act as biological flocculators, to physically change the influent COD, soluble and particulate, to a form that allows effective liquid solid separation. In the conventional short sludge age plant the waste sludge is transferred to the sludge treatment facility; in the aerated lagoon usually a second pond is provided i.e. an oxidation pond or a facultative aerated lagoon, to allow the now readily settleable particulate material to settle as a sludge layer and thereby produce a relatively solids-feee effluent.

Aerated lagoons find application principally in industrial waste treatment and seasonal waters. Design considerations are not dealt with in this manual; these are discussed by Marais and Ekama (1980) and reference should be made to that report.

11.2 Intermediate Sludge Ages (10-15 days)

Where nitrification is obligatory, the sludge ages required are 5 to 8 times longer than those for COD removal only, depending on the

temperature. In the temperate regions where water temperatures may fall below 12°C to 14°C the sludge age is unlikely to be less than 10 to 15 days. In this range of sludge age, the effluent COD concentration no longer plays a rôle in the design because for sludge ages longer than about 4 days, the effluent COD or BOD concentrations remain approximately constant (see Section 3.4 above). The effluent ammonia concentration also plays a minor rôle in design because nitrification kinetics are such that once nitrification is achieved, it is virtually complete; even though the effluent standards may require an effluent ammonia concentration of less than, say, 10 mgN/ℓ, once nitrification takes place the concentration is likely to be less than 4 mgN/ℓ. Consequently for nitrification, the sludge age of the process is fixed completely by the requirement for nitrification. (The method for calculating the minimum sludge age for nitrification is given in Chapter 5, Section 4.)

With low alkalinity wastewaters (like those encountered in the Western and Southern Cape), nitrification can cause a significant reduction in effluent pH, often as low as 5. This not only causes problems with the nitrification process itself in that only partial nitrification is achieved, with the likelihood of non compliance of the 10 mgN/ℓ effluent ammonia standard (see Chapter 5, Section 4.3), but it also tends to favour the development of poor settling sludges and to produce aggressive effluents that can do considerable damage to concrete surfaces. To reduce these problems (and to derive other advantages cited later in this section) the policy of deliberate biological denitrification has evolved. However, once biological denitrification is incorporated in the process, sludge ages longer than 10 to 15 days are required and the process falls into the long sludge age category.

Comparing intermediate sludge age plants with high rate plants, the oxygen demand per kgCOD (including nitrification) is doubled (see Fig 6.1), the process volume is 3 to 4 times larger (see Fig 4.3), the daily sludge mass wasted is reduced by 40% (see Fig 4.4) and active fraction is much lower (see Fig 4.2). Intermediate sludge age plants

are much more stable than high rate plants, requiring less sophisticated control techniques or operator intervention thereby making these plants more suitable for general application.

At intermediate sludge ages, the active fraction of the waste sludge is still too high for direct discharge to drying beds. Consequently some form of waste sluge stabilization would need to be incorporated in the treatment works, i.e. either aerobic or anaerobic digestion. The former has the advantage of ease of operation but the disadvantage of energy costs for oxygen supply; the latter has the advantage of energy production but the disadvantage of complexity of operation. Even with energy recovery by anaerobic digestion of waste sludge, because of the low mass of sludge wasted from the activated sludge plant and high oxygen demand per kgCOD load, energy self-sufficiency at intermediate sludge ages is impossible. However, on large plants (± half million person equivalent) where technical supervision and operator expertise are of a high level, energy cost can be reduced by gas production from anaerobic digestors and probably can be justified economically, particularly if energy costs continue to increase as they have over the past decade.

In nitrifying aerobic activated sludge plants, there is always the possibility that denitrification can take place in the secondary settling tank. This problem is exacerbated by the process control procedure of abstracting the waste sludge from the settling tank underflow (see Section 10 above). This procedure is used to benefit from the thickening function of the settling tank: the lower the underflow recycle ratio, the higher the underflow concentration, the lower the volume of waste sludge. However low underflow recycle ratios result in large sludge accumulations in the secondary settling tank (see Fig 4.8). Hence the sludge might be retained in the settling tank for a long period of time and this is likely to lead to denitrification. The degree of denitrification is increased as

(i) the residence time in the settling tank increases - this depends on the recycle ratio and peak flow conditions.

(ii) the active fraction of the sludge increases, i.e. is greater at shorter sludge ages, Fig 4.2;

(iii) the temperature increases; and

(iv) the mass of biodegradable COD adsorbed on the organism mass increases (van Haandel, Ekama and Marais, 1981) - this is generally greatest at the peak load condition.

If denitrification in the settling tank takes place to a sufficient degree, attachment of sludge particles to the nitrogen gas bubbles causes buoying of the particles to the surface. The flotation effect can cause considerable loss of sludge via the settling tank overflow. This behaviour has been observed, for example, at Bellville, Cape Town, where sludge losses have been observed during that latter part of summer when the water temperatures are around 22°C. Sludge loss occurs daily in the afternoon after the peak flow and load when both the sludge accumulation in the settling tank and stored COD adsorbed on the sludge mass are at a maximum. Although the underflow recycle ratio is quite high (s = 2) sufficient sludge still accumulates to make denitrification significant at high temperatures.

The above discussion on experience with nitrifying activated sludge plants points to the following conclusions -

The secondary settling tank no longer should serve the dual purpose of solid-liquid separation and thickening. The sludge residence time needs to be minimized, to reduce denitrification, by having a high underflow recycle ratio, of 1 to 2:1, but this will result in inadequate thickening of the waste sludge withdrawn from the underflow. The thickening aspect can be solved by implementing hydraulic control of the sludge age, by providing a small independent satellite settling tank for gravity thickening of the waste sludge (the supernatant being returned to the reactor so that inadequate clarification due to denitrification flotation does not affect effluent quality) or by replacing the gravity satellite tank with a dissolved-air flotation unit.* These modifications, however, ameliorate the effects on the secondary settling tank but do not positively remove the root cause,i.e. the high nitrate concentration in the mixed liquor. This can be done

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* Thickening by dissolved air flotation now is both technically and economically feasible, Bratby and Marais (1976, 1977).

only by including denitrification in the process, which then shifts the process to that of the long sludge age type.

11.3 Long Sludge Ages (20 days or more)

Aerobic plants: Long sludge age aerobic plants are usually called extended aeration plants. The sludge age is chosen so long that the active mass fraction of the waste sludge is sufficiently reduced to allow discharge directly to sludge drying beds after thickening. What this sludge age should be will depend to a degree on the climatic conditions i.e. whether the sludge can be dried before it starts smelling, but probably exceeds 30 to 40 days - research into the sludge ages necessary under South African conditions is necessary.

Compared to intermediate sludge age plants the total oxygen demand (i.e. carbonaceous plus nitrification) is about equivalent (Fig. 6.1); the process volume requirement is 50 to 60% higher and the active fraction 50% lower. As nitrification always occurs, problems with rising sludge in the settling tank are to be expected. Control of the sludge age is best via the hydraulic sludge age control method, so that high recycles from the secondary settling tank can be imposed to reduce rising sludge in the tank, as described under intermediate sluge age processes above. Problems of low pH when treating low Alkalinity wastewater are to be expected.

Extended aeration plants are very stable in operation and require probably less supervision than any other activated sludge process. Although the volume requirements and the oxygen demand per unit input COD is large, the relative ease of operation makes this process the indicated one for small communities. However, it must be remembered that this process will discharge a low COD effluent but with high nitrate and phosphate concentrations. The nitrate concentration can be drastically reduced and low pH effluent prevented by incorporating an anoxic zone in the process without basically disturbing the ease of operation. This modification always should be kept in mind when considering extended aeration as a possible process.

Processes that can be operated in the extended aeration modes are

the completely mixed single reactor, the Orbal multi-channel, oxidation ditch and Carrousel processes.

Anoxic-Aerobic Process

Once sludge ages in the range greater than 20 days are accepted it is possible usually to incorporate denitrification in the process without upsetting stability in nitrification. The reactor is suitably subdivided into unaerated (anoxic) and aerated zones in a variety of ways, the denitrification taking place in the unaerated zones and the nitrification in the aerated zones to give the so-called nitrification-denitrification process. The advantages are substantial: (1) Nitrate concentration in the effluent is reduced, the nitrate utilized in the unaerated zones lowering the oxygen demand of the process accordingly; with complete denitrification the total oxygen demand can be reduced by approximately 15 to 20% compared with the requirements for a nitrifying process. (2) Loss of sludge in the overflow from the settling tank due to rising sludge is largely eliminated , and (3) alkalinity recovery with denitrification makes that pH instability with low influent alkalinity wastewaters is very unlikely, Normally the sludge ages in nitrification-denitrification plants are insufficient to allow direct discharge of the waste sludge to the drying beds.

Process configurations of anoxic-aerobic system are the Modified Ludzack-Ettinger process in which a primary anoxic reactor is provided, the Bardenpho which incorporates both primary and secondary anoxic reactors, the Orbal in which anoxic zones are created by reducing the aeration energy input in channels, Carrousel and oxidation ditch in which the aeration at the aerators is controlled to induce anoxic zones between the aeration points, and sequential aeration and anoxic operation in the same reactor, or in two interlinking parallel reactors.

Incorporation of biological denitrification in a process imposes additional constraints on the design. It requires the selection of a process sludge age *and* an unaerated mass fraction, (to achieve the required denitrification or the highest denitrification possible), yet ensuring efficient nitrification under all expected conditions. (See Chapter 5, Section 6, and Chapter 6, Section 6).

Anaerobic-anoxic-aerobic systems

These plants are needed where biological removal of both nitrogen and phosphorus is required and are called biological excess P removal plants. The phosphorus removal propensity is created by providing a zone in the process that receives the influent wastewater but no oxygen and nitrate (via the recycles of mixed liquor). The incorporation of this zone imposes further constraints on the design of the system: A sludge age must be selected that will ensure efficient nitrification at all times, provide for anoxic zones that will give complete or maximal removal of nitrate and an anaerobic zone that receives the influent flow and recycles of mixed liquor not containing nitrate generated in the system. The critical aspects of the design are the assurance of nitrification and the assurance of no discharge of nitrate to the anaerobic zone. The success of the design is sensitive to a number of factors: the influent wastewater characteristics, such as the readily biodegradable COD concentration, the TKN/COD and P/COD ratios, the maximum specific growth rate of the nitrifiers, maximum and minimum temperatures, severity of cyclic load and flow, control of aeration and control of nitrate and dissolved oxygen in some of the recycles.

Aeration control is a particularly vexing problem under cyclic load and flow conditions because the process is affected by too high or too low oxygen concentrations in the aerobic zone. Too high concentrations cause oxygen to be recycled to the anoxic zone (and the anaerobic zone in the 5 stage Phoredox process), thereby reducing the potential for P and N removal; too low oxygen concentrations cause the nifrification efficiency to decline and poor settling sludges to develop.

Oxygen control setups that have been developed still require considerable operational attention, particularly the oxygen probes, and at present their installation in smaller plants is to be questioned. These difficulties have prompted research into an alternative solution - load and flow equalization. In this approach an equalization tank is provided upstream of the plant. The effluent flow from the tank is controlled in such a manner that the cyclic fluctuations in the flow *and* load are damped to very small values. The control is via a microcomputer that calculates the discharge flow setting. The essential inputs to the computer are the depth of liquor in the equalization tank and the flow rate out of the tank; both these measurements can be readily monitored automatically and operate reliably over long periods of time. The microcomputer also has reached a stage of development that ensures its long term trouble-free service. The equalization approach with the microcomputer control, has been tested at Goudkoppies plant, Johannesburg and shows great potential for reducing aeration and other control problems in nutrient removal plants. Detailed information on equalization tanks is available in a report by Dold, Buhr and Marais (1982). Design details of the P removal processes, considered in this Manual, are given in Chapter 7.

It should be noted that the waste sludge from a biological excess removal activated sludge process contains high concentrations of P. If the sludge is allowed to become anaerobic or is anaerobically digested much of the phosphorus removed from the wastewater will be released from the sludge mass to the bulk liquid, consequently seepage from drying beds may have to be chemically treated to precipitate the phosphorus before recycling to the plant. Failure to recognize this behaviour of phosphorus rich biological sludges may lead to inadvertent re-contamination of the effluent with high concentrations of phosphorus (see Section 8 above).

Examples of N and P removal processes are the multi-reactor Phoredox and UCT processes in which the anaerobic, anoxic and aerobic conditions

are induced in separate reactors interlinked by recycle flows. Other removal systems have been proposed, for example that by Kerdachi and Roberts (1982) in which these conditions are imposed within the same reactor.

Where P removal without obligatory nitrogen removal is required the sludge age can be selected to prevent nitrification and in the multi-reactor type plant theoretically only anaerobic and aerobic reactors are needed, i.e. no anoxic reactor. The sludge age is reduced substantially, probably to less than eight days, so that the reactor volume per input COD is much smaller than where nitrification-denitrification is a requirement. However, even with these short sludge ages it would be wise, always, to make provision for denitrification of any nitrate generated and recycled to the anaerobic zone. This provision is of particular relevance in warm climates or where the maximum specific growth rate of the nitrifiers is very high so that nitrification can occur at *aerobic* sludge ages of, say, 2 days. These short sludge age P removal plants are not considered in this manual.

12. DESIGN EXAMPLE

In this section, the procedure for design of organic material (COD) degradation in purely aerobic processes is demonstrated with numerical examples. Assuming flow and load conditions, calculations are presented showing how estimates of the process volume requirements, average daily carbonaceous oxygen demand and daily sludge production are obtained for the treatment of raw or settled wastewaters based on the wastewater characteristics.

12.1 Influent Wastewater Characteristics

The daily average characteristics for a particular raw wastewater are given in Table 4.3. In the design example it is assumed that primary sedimentation tanks remove 40% of the total COD load, 15% of the TKN and total P and 10% of the readily biodegradable COD. The settled wastewater characteristics are also given in Table 4.3. It should be noted that the *soluble concentrations* in the settled wastewater should be approximately equal to those in the raw wastewater. For example, from Table 4.3 the soluble unbiodegradable COD

concentration in the raw wastewater is 0,5 mg COD/mg COD, i.e. 0,05.600 = 30 mg COD/ℓ (Eq. 2.3). As the soluble unbiodegradable constituents are not affected by primary sedimentation, the unbiodegradable soluble COD *fraction* of the settled wastewater accordingly will be approximately 30/360 = 0,08 mg COD/mg COD. Similarly, the readily biodegradable COD fraction (f_{bs}) of the raw waterwater is given as 0,24. This is equivalent to a concentration of 0,24 (1 - f_{up} - f_{us})S_{ti} = 0,24(0,82)600 = 118 mg COD/ℓ (see Eqs. 2.8 and 2.9). Primary sedimentation is assumed to remove 10% of the readily biodegradable COD (due to biodegradation), the f_{bs} *fraction* in the settled wastewater is given by {(1,0 - 0,10)118}/{(1 - 08 - 0,04)360} = 0,33 (see Eqs. 2.8 and 2.9). The examples show that care must be taken that settled wastewater characteristics are not fixed at values that are inconsistent with the raw wastewater characteristics and primary settling tank behaviour.

Table 4.3 Raw and settled wastewater characteristics (see also Tables 5.2 and 6.1).

Parameter	Symbol	Value		Units
		Raw	Settled	
Influent COD concentration	S_{ti}	600*	360*	mgCOD/ℓ
Influent TKN concentration	N_{ti}	48*	41*	mgN/ℓ
Influent P concentration	P_{ti}	10	8,5*	mgP/ℓ
TKN/COD ratio	-	0,080	0,114	mgN/mgCOD
P/COD ratio	-	0,017	0,024	mgP/mgCOD
Unbiodegradable soluble COD	f_{us}	0,05	0,08	mgCOD/mgCOD
Unbiodegradable particulate COD	f_{up}	0,13	0,04	mgCOD/mgCOD
MLVSS/MLSS ratio of sludge produced	f_i	0,75	0,83	mgVSS/mgTSS
Temperature - Summer	T_{max}	22	22	°C
- Winter	T_{min}	14	14	°C
pH of wastewater	-	7,5	7,5	-
Influent flow	Q	13,33	13,33	Mℓ/d

*Influent concentrations appropriately weighted to take account of daily cyclic flow variations

12.2 Temperature Effects

From Table 4.1, the only constant in the organic material degradation theory that is affected by temperature is the endogenous respiration rate, b_h. This rate reduces by about 3% every 1°C drop in temperature - from Eq (4.5), (given in Table 4.1), the rate at 14°C is 0,20/d and at 22°C is 0,25/d. The effect of the reduction in the rate with decrease in temperature is that at reduced temperatures the daily sludge production is marginally increased and the average carbonaceous oxygen demand is marginally decreased - the differences in sludge production and oxygen demand are less than 5% for a 6°C change in temperature. Consequently, the average carbonaceous oxygen demand should be calculated at the maximum temperature and the process volume and sludge production at the minimum temperature in order to find the maximum values of these parameters.

12.3 Calculations for Organic Material Degradation

The example will demonstrate the effect of temperature and sludge age on (i) the mass of sludge in the process, (ii) the average daily carbonaceous oxygen demand, (iii) the active fraction of the sludge and (iv) mass of sludge wasted daily. These four parameters will be calculated for the raw and settled wastewater at 14°C and 22°C for sludge ages ranging from 5 to 30 days. The values of the constants Y_h, f_{cv}, f and b_h (appropriately adjusted for temperature) are given in Table 4.1.

Mass of COD treated/d $= M(S_{ti}) = Q.S_{ti}$ (4.6)

Mass of biodegradable COD $= M(S_{bi}) = (1-f_{up}-f_{us})M(S_{ti})$ (4.7c)

Mass of unbiodegradable particulate solids

$$M(X_{ii}) = M(S_{ti})f_{up}/f_{cv} \quad (4.8c)$$

Hence for raw wastewater:

$M(S_{ti})$ = 13,33.10 .600 mg COD/d = 8000 kg COD/d

f_{us} = 0,05 mg COD/mg COD

f_{up} = 0,13 mg COD/mg COD

$M(S_{bi})$ = (1 - 0,05 - 0,13)8000 = 6560 kg COD/d

$M(X_{ii})$ = 8000.0,13/1,48 = 702,7 kg VSS/d

and for settled sewage:

$M(S_{ti})$ = 60% of 8000 = 4800 kg COD/d

f_{us} = 0,08 mg COD/mg COD

f_{up} = 0,04 mg COD/mg COD

$M(S_{bi})$ = (1 - 0,08 - 0,04)4800 = 4724 kg COD/d

$M(X_{ii})$ = 4800.0,03.1,48 = 97,3 kg VSS/d

From Eq (4.13) the mass of volatile solids in the process is given by

$$M(X_v) = \frac{0,45\ R_s\ M(S_{bi})}{(1 + b_{hT}\ R_s)}\ (1 + 0,2\ b_{hT}\ R_s) + M(X_{ii})\ R_s$$

$$= \frac{2952\ (1 + 0,2\ b_{hT}\ R_s)}{(1 + b_{hT}\ R_s)} + 702,7\ R_s \qquad (4.29a)$$

for raw wastewater.

$$M(X_v) = \frac{1901\ (1 + 0,2\ b_{hT}\ R_s)}{(1 + b_{hT}\ R_s)} + 97,3\ R_s \qquad (4.29b)$$

for settled wastewater.

From Eq (4.14) the mass of Total Suspended Solids in the process is given by

$$M(X_t) = M(X_v)/0,75 \text{ for raw wastewater} \quad (4.30a)$$

$$= M(X_v)/0,83 \text{ for settled wastewater} \quad (4.30b)$$

From Eq (4.15), the average daily carbonaceous oxygen demand is given by

$$M(O_c) = M(S_{bi}) \{(1-f_{cv}Y_h) + f_{cv}(1-f)b_{hT} \frac{Y_h R_s}{(1+b_{hT} R_s)}\}$$

$$= 6560 \{(0,334) + 0,533 \frac{b_{hT} R_s}{(1+b_{hT} R_s)}\} \text{ (kg O/d)} \quad (4.31a)$$

for raw wastewater.

$$= 4224 \{(0,334 + 0,533 \frac{b_{hT} R_s}{(1+b_{hT} R_s)}\} \text{ (kg O/d)} \quad (4.31b)$$

for settled wastewater.

From Eq (4.18), the active fraction with respect to the volatile suspended solids (f_{av}) is given by

$$f_{av} = 1/\{1+0,2\ b_{hT} R_s + 0,238\ (1+b_{hT} R_s)\}$$

$$= 1/\{1,238+0,438\ b_{hT} R_s\} \text{ for raw wastewater.} \quad (4.32a)$$

$$= 1/\{1+0,2\ b_{hT} R_s + 0,068\ (1+b_{hT} R_s)\}$$

$$= 1/\{1,068+0,268\ b_{hT} R_s\} \text{ for settled wastewater} \quad (4.32b)$$

From Eq (4.22), the mass of sludge (as Total Suspended Solids) produced per day is given by

$$M(\Delta X_t) = \frac{8000}{0,75} \{\frac{0,82.0,45}{(1+b_{hT} R_s)}\ (1+0,2\ b_{hT} R_s) + \frac{0,13}{1,48}\}$$

$$= 10667\{\frac{0,369\ (1+0,2\ b_{hT} R_s)}{(1+b_{hT} R_s)} + 0,09\} \quad (4.33a)$$

for raw wastewater.

$$M(\Delta X_t) = \frac{8000}{0,83}\left\{\frac{0,88.0,45}{(1+b_{hT}\ R_s)}\ (1+0,2\ b_{hT}\ R_s) + \frac{0,04}{1,48}\right\}$$

$$= 5783\left\{\frac{0,396\ (1+0,2\ b_{hT}\ R_s}{(1+b_{hT}\ R_s)} + 0,03\right\} \qquad (4.33b)$$

for settled wastewater.

Substituting the b_{hT} value for 14°C (i.e 0,202/d) and 22°C (i.e 0,254/d) into Eqs (4.25 to 4.29) the parameters $M(X_v)$, $M(X_t)$, $M(O_c)$, f_{av} and $M(\Delta X_t)$ can be calculated for sludge ages 5 to 30 days. The results are shown plotted in Fig 4.9.

Figure 4.9 confirms that the mass of sludge in the process (MLSS or MLVSS), the average carbonaceous oxygen demand and the active fraction (with respect to MLSS or MLVSS) are only marginally affected by temperature and for these parameters insofar as design is concerned, are not really of consequence. However, the influent waste type i.e. raw or settled wastewater, has a significant effect; raw wastewater results in more sludge in the process, a higher oxygen demand and a lower active fraction of the sludge than settled wastewater. The difference in effects between raw and settled wastewater depends wholly on the efficiency of the primary settling tanks - the differences apparent in Fig. 4.9 arise from a 40% COD removal in primary sedimentation. The greater the efficiency of primary sedimentation the greater the difference between the parameters shown in Fig. 4.9

From Eq. (4.16) for the same MLSS concentration, the process volume is proportional to the mass of sludge contained in it. Hence for the same MLSS concentration, the volume of the process treating settled wastewater will be only 40% of that treating raw wastewater at 25 days sludge age. Also, the settled wastewater plant requires only 64% of the oxygen the raw wastewater plant requires. However, the active fraction of the sludge in the settled wastewater plant is 34%, probably too high for direct discharge to the drying beds, whereas that from the raw wastewater plant is 22%, probably sufficiently low for discharge to drying beds without further stabilization. Clearly the

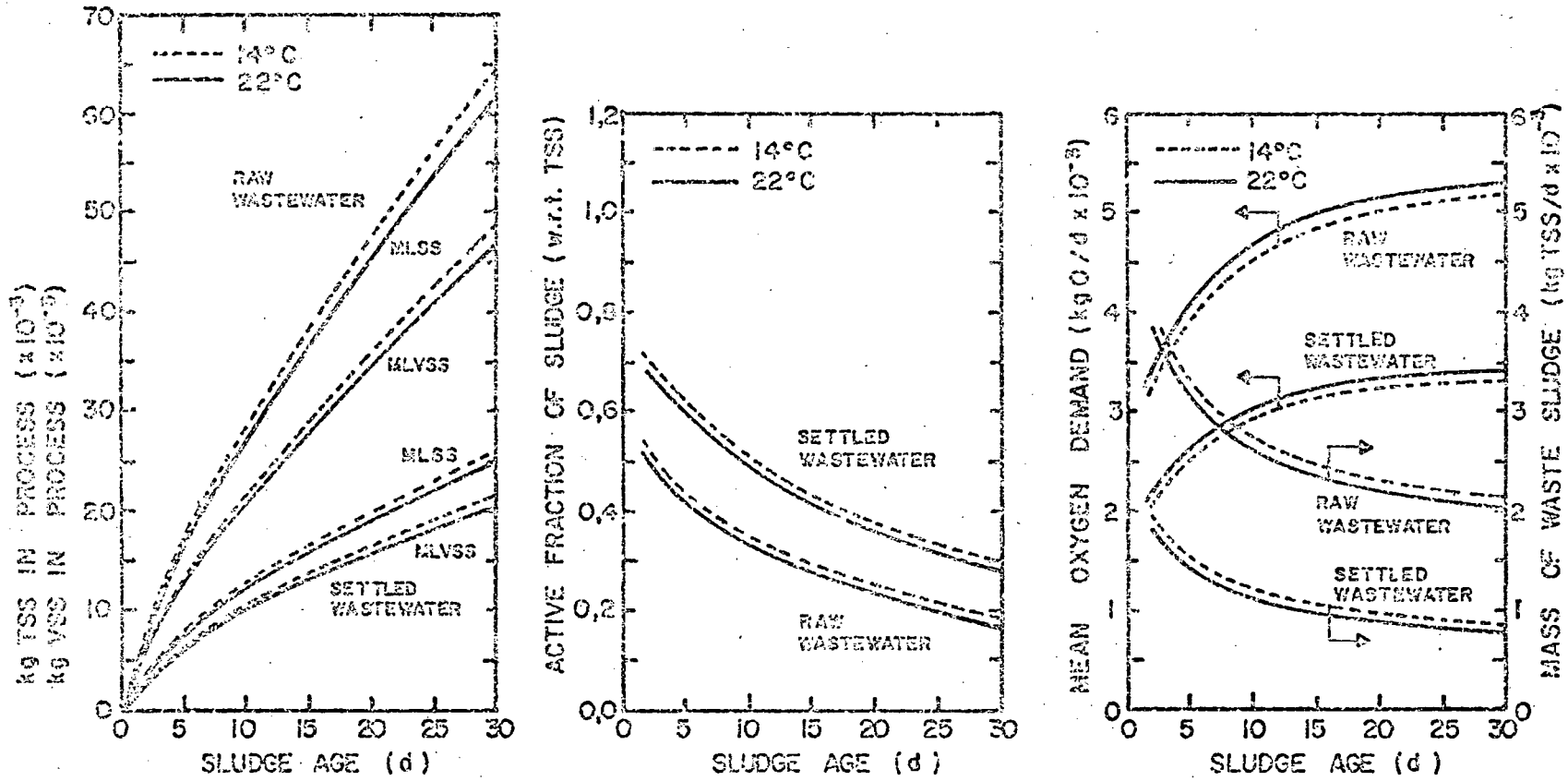

Fig 4.9 *Mass of sludge (MLSS and MLVSS), active fraction (with respect to TSS), average carbonaceous oxygen demand and mass of sludge (as TSS) produced daily versus sludge age for raw and settled wastewaters at 14°C and 22°C. Wastewater*

choice of treating settled sewage as against raw sewage requires weighing the advantages and disadvantages of each against each other, i.e. settled sewage (smaller process volume, smaller oxygen demand and smaller secondary sludge production, but, with primary sludge production and its disposal) against raw sewage (greater process volume, higher oxygen demand and higher secondary sludge production, but no primary sludge production). The choice is made more difficult by the fact that higher biological removals of N and P are achieved with raw wastewater than with settled wastewaters (see Chapter 3, Section 5). These aspects are discussed in detail in Chapters 6 and 7 and will be demonstrated by extending the above design example to include biological nitrogen and phosphorus removal.

13. CONCLUSIONS

The calculations for the daily sludge production, daily average carbonaceous oxygen demand, process volume and nitrogen and phosphorus requirements for sludge production etc. were demonstrated for a raw and a settled sewage with selected wastewater characteristics for the raw sewage and assumed effects of primary settlement on the raw sewage characteristics. Selection of the numerical magnitudes of these characteristics was based on experience with five municipal waste flows so that the data should not be taken to apply generally. Whenever possible, the characteristics should be determined experimentally, or estimated by some semi-experimental procedure supplemented by experience. Where design information is inadequate it will be necessary to select ranges of values for some parameters, ranges that appear to span across the true values, and to repeat the design a number of times using various combinations of the limiting values. In this way a picture will be built up of the sensitivity of the plant process response so that appropriate provisions can be made in the design. There are so many interactive effects that ample design provision in one aspect, for example, does not necessarily resolve that problem in terms of the whole design as it may create problems in other aspects.

14. REFERENCES

1. Arkley M and G v R Marais (1982). Effect of the anoxic sludge mass fraction on the activated sludge process. Research Report No. W 38, Dept. of Civil Eng., Univ. of Cape Town.

2. Bratby J and G V R Marais (1976). A guide for the design of dissolved-air (pressure) flotation systems for activated sludge processes. Water SA, 2, 2, 86-100.

3. Bratby J and G v R Marais (1978). Aspects of sludge thickening by dissolved-air flotation. Wat.Pollut.Control, 77, 3, 421-432.

4. Dold P L, G A Ekama and G v R Marais (1980). A general model for the activated sludge process. Prog.Wat.Tech., 12, 47-77.

5. Dold P L, H O Buhr and G v R Marais (1982). Design and control of equalization tanks. Research Report No. W 42, Dept. of Civil Eng., Univ. of Cape Town.

6. Ekama G A and G v R Marais (1978). The dynamic behaviour of the activated sludge process. Research Report No. W 27, Dept. of Civil Eng., Univ. of Cape Town.

7. Garrett M T (1958). Hydraulic control of activated sludge growth rate. Sew. and Ind. Wastes, 30, 253.

8. Marais G v R and G A Ekama (1976). The activated sludge process part 1 - steady state behaviour. Water SA, 2, 4, 163-200.

9. Marais G v R and G A Ekama (1980). Aerated lagoons. Research Report, Dept. of Civil Eng., Univ. of Cape Town.

10. McKinney R E and J M Symons (1964). Growth and endogenous metabolism - a discussion. Proc. 1st Int.Conf. on Wat. Pollut. Control, London, 1962, Pergamon Press, Oxford.

11. Nicholls H A (1975). Internal Thesis Report, Dept. of Civil Eng., Univ. of Cape Town.

12. Payne W J (1970). Energy yields and growth of heterotrophs. Annual reviews - microbiology, 17-51.

13. Sehayek E and G v R Marais (1981). Kinetics of biological nitrogen removal in the single sludge activated sludge process. Research Report No. W 41, Dept. of Civil Eng., Univ. of Cape Town.

14. Setter L R, W T Carpenter and G C Winslow (1945). Practical application of modified sewage aeration. Sew.Works Jour. 17, 4, 669.

15. van Haandel A C, G A Ekama and G v R Marais (1981). The activated sludge process - 3 - single sludge denitrification. Water Research, 15, 1135-1152.

16. van Haandel A C and G v R Marais (1981). Nitrification and denitrification in the activated sludge process. Research Report No. W 39, Dept. of Civil Eng., Univ. of Cape Town.

CHAPTER FIVE

NITRIFICATION

by

G A Ekama and G v R Marais

1. INTRODUCTION

The term nitrification describes the biological process whereby free and saline ammonia is oxidized to nitrite and nitrate. Nitrification is mediated by *specific autotrophic organisms* with behavioural characteristics that differ significantly from the heterotrophic ones. The objectives in this chapter are to review briefly the kinetics of nitrification, to highlight the factors that influence this biological reaction and set out the procedure for designing a nitrifying-aerobic activated sludge process.

It has been well established that nitrification is due to two specific genera of autotrophic bacteria, the *Nitrosomonas* and *Nitrobacter*. Nitrification takes place in two sequential oxidation steps: (1) *Nitrosomonas* convert free and saline ammonia to nitrite, and (2) *Nitrobacter* convert nitrite to nitrate. The nitrifiers utilize ammonia for their synthesis nitrogen requirements, and as a source of energy to bring about synthesis. The ammonia requirement for synthesis, however, is a negligible fraction of the total ammonia processed by the organisms, at the most 2% (van Haandel and Marais, 1981). Consequently it is usual to neglect the metabolic nitrogen requirements* of the nitrifiers and to consider the nitrifiers simply to act as catalysts for the ammonia-nitrite-nitrate reactions - the reactions are taken as stoichiometric. This greatly simplifies the description of the kinetics of the process.

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*In nitrification processes, where the influent energy source consists principally of ammonia, this simplification no longer can be applied and the determination of the nitrifying sludge mass is necessary to design the process volume (Neytzel-de-Wilde, 1977). With municipal wastes under *cyclic* flow conditions the nitrifying mass also needs to be calculated.

Consider the two basic redox reactions in nitrification,

$$NH_4^+ + 3/2\ O_2\ (\textit{Nitrosomonas}) \rightarrow NO_2^- + H_2O + 2H^+ \qquad (5.1a)$$

$$NO_2^- + 1/2\ O_2\ (\textit{Nitrobacter}\ ) \rightarrow NO_3^- \qquad (5.1b)$$

Stoichiometrically the oxygen requirements for the first and second reactions are 3,43 and 1,14 mgO/mgN [also written as mgO/mg(NH_3-N)]. Hence the conversion of ammonia to nitrate, both expressed as N, requires 4,57 mgO/mgN utilized. Taking into account the ammonia utilized for metabolic purposes of the nitrifiers, the oxygen requirements per mg(NH_3-N) processed are slightly less, with reported values down to 4,3 mgO/mg(NH_3-N). However such a sophisticated approach is more of academic than practical interest and we will accept the stoichiometric value, 4,57 mgO/mg(NH_3-N).

2. BIOLOGICAL KINETICS

2.1 Growth

In order to formulate the nitrification behaviour it is necessary to understand the basic biological growth kinetics of nitrification. Here one has to consider the two stage nitrification behaviour. The rate of conversion of ammonia to nitrate, by the *Nitrosomonas* is much slower than that of nitrite to nitrate, by the *Nitrobacter*. In fact, under most circumstances in municipal wastewater treatment plants, any nitrite that is formed is converted virtually immediately to nitrate. As a consequence very little nitrite is observed in the effluent from a plant operating on an influent that does not contain substances that inhibit the *Nitrobacter*. The limiting rate in the nitrification sequence, therefore, is that due to the *Nitrosomonas* - one needs to consider the kinetics of this organism only. Because the nitrite produced is virtually immediately converted to nitrate in terms of the growth rate of the *Nitrosomonas*, to assume that the conversion is from ammonia to *nitrate* directly - on this basis the kinetics of nitrification reduce to the kinetics of the *Nitrosomonas*.

Experimental investigations by Downing, Painter and Knowles (1964) showed that the nitrification rate can be formulated in

terms of Monod's relationship. Monod found that (1) The mass of organisms generated is a fixed fraction of the mass of substrate (in this case ammonia) utilized. (2) The *specific rate of growth*, that is, the rate of growth per unit mass of organisms per unit time, is related to the concentration of substrate surrounding the organisms.

From (1)

$$M(\Delta X_n) = Y_n \, M(\Delta N_a) \tag{5.2}$$

where

$M(\Delta X_n)$ = mass of nitrifiers generated, (mgVSS)

$M(\Delta N_a)$ = mass of ammonia as N utilized, [mg(NH_3-N)]

Y_n = mass of nitrifiers generated per unit mass of ammonia utilized, [mgX_n/mg(NH_3-N)]

Consequently one can write

$$\frac{dX_n}{dt} = Y_n \frac{dN_a}{dt} \tag{5.3}$$

From (2) Monod developed the following relationship,

$$\mu_{nT} = \frac{\mu_{nmT} \, N_a}{K_{nT} + N_a} \tag{5.4}$$

μ_n = specific growth rate observed at concentration N_a, (mgX_n/mgX_n/d)

μ_{nm} = maximum specific growth rate possible (mgX_n/mgX_n/d)

K_n = half saturation constant, i.e. the concentration at which $\mu = \frac{1}{2} \mu_{nm}$

N_a = concentration of ammonia surrounding the organisms, [mg(NH_3-N)/ℓ]

T subscript refers to temperature, (deg.C)

The *growth rate* is given by the product of the specific growth rate and the organism mass

$$\frac{dX_n}{dt} = \mu_{nT} \cdot X_n = \frac{\mu_{nmT}\, N_a}{K_{nT} + N_a} \cdot X_n \qquad (5.5)$$

Instead of expressing the growth rate in terms of the mass of organisms, it is often useful also to express it in terms of the depletion rate of ammonia, as follows: From Eq (5.3) substituting for dX_n/dt in Eq (5.5)

$$\frac{dN_a}{dt} = \frac{(\mu_{nmT}/Y_n)N_a}{K_{nT} + N_a} X_n \qquad (5.6)$$

Equation (5.6) is sometimes written in an equivalent form as follows: Define the maximum specific substrate utilization rate, $K_{mT} = \mu_{nmT}/Y_n$ then the specific substrate utilization rate K_T becomes from Eq (5.4)

$$K_T = \frac{K_{mT}\, N_a}{K_{nT} + N_a} \qquad (5.7)$$

and the rate of substrate utilization, from Eq (5.6)

$$\frac{dN_a}{dt} = \frac{K_{mT}\, N_a}{K_{nT} + N_a} \cdot X_n \qquad (5.8)$$

This form is mentioned here because it is the one often used to express heterotrophic growth, and in fact is the form utilized in all the work published by the Marais group, because of its greater convenience for some purposes. The point to note is that Eqs (5.6 and 5.8) are of equal merit.

The ammonia nitrogen that disappears in the nitrification reaction, reappears as nitrate nitrogen because the stoichiometric approach is adopted, i.e.

$$\frac{dN_n}{dt} = \frac{dN_a}{dt} \tag{5.9}$$

Consequently

$$\frac{dN_n}{dt} = \frac{(\mu_{nmT}/Y_n)N_a}{K_{nT} + N_n} .X_n \tag{5.10}$$

where

N_n = nitrate concentration, $(mg(NO_3\text{-}N)/\ell)$.

The oxygen consumption associated with nitrification is based on the stoichiometric assumption mentioned earlier, i.e. conversion of $1mg(NH_3\text{-}N)$ to $1mg(NO_3\text{-}N)$ requires 4,57 mgO. Consequently

$$\frac{dO_n}{dt} = 4,57 \frac{dN_a}{dt} \tag{5.11}$$

2.2 Endogenous Respiration

Up to this stage attention has been focussed on the growth aspect. However, Herbert (1958) showed that generally an organism mass undergoes a continuous mass loss, called endogenous mass loss. Furthermore from the great amount of research undertaken by the Marais group it seems that this loss occurs independently of the growth. This allows straightforward formulation of endogenous mass loss as,

$$\frac{dX_n}{dt} = -b_{nT} X_n \tag{5.12}$$

where

b_{nT} = specific endogenous mass loss rate for *Nitrosomonas* (mg/mg/d)

2.3 Behavioural Characteristics

In Fig (5.1) are shown the relationship between the specific growth rate, μ_n, the specific substrate utilization rate, K, and

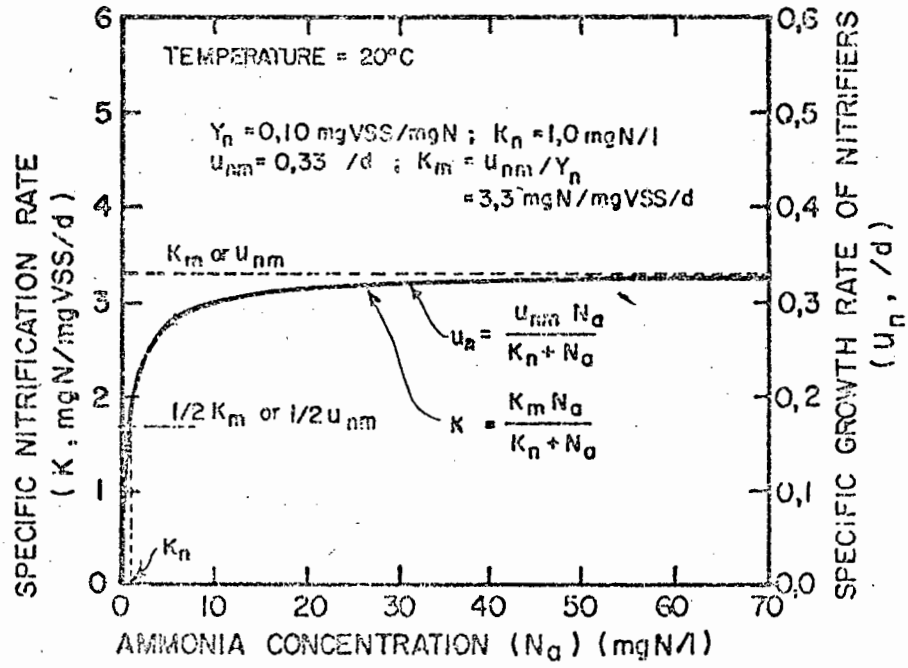

Fig 5.1 *Monod's relationship for nitrification at 20°C.*

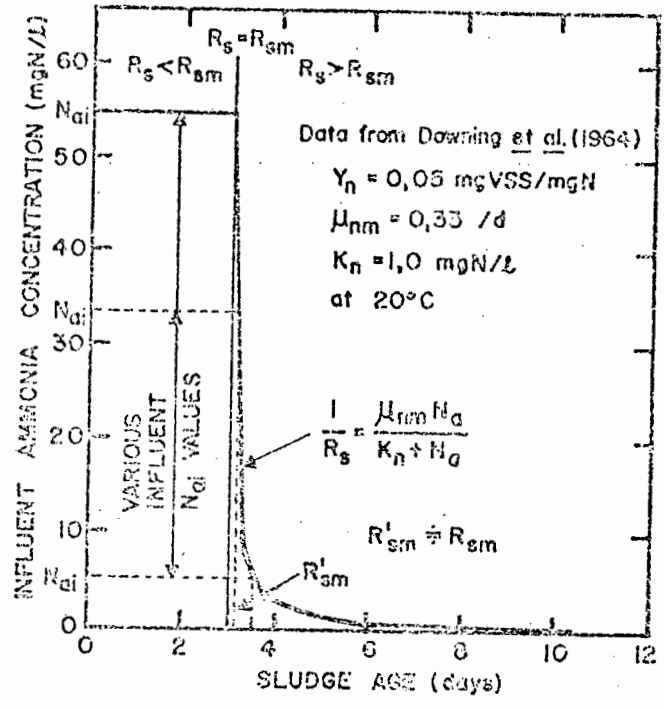

Fig 5.2 *Relationship between sludge age for nitrification and influent ammonia concentration, N_{ai}.*

the substrate concentration, N_a, as described by Monod's equation Eqs (5.4 and 5.7) respectively. The rate constants selected are $\mu_{nm20} = 0{,}33$, $Y_n = 0{,}10$ (hence $K_m = 3{,}3$) and $K_{n20} = 1{,}0$. The interesting feature of this plot is that, because K_n is so small $\cong$ 1 mg(NH_3-N)/ℓ, the specific rate is virtually at a maximum for concentrations of 2 mg(NH_3-N)/ℓ and higher. However at concentrations less than two the rate rapidly declines to zero so that the ammonia is not readily reduced to zero.

3. PROCESS KINETICS

As indicated in Chapter 4 the basic process unit is the completely mixed activated sludge unit. The process under steady state provides the information necessary for design.

With regard to nitrification, for design, the principal steady state solution required is that of the effluent ammonia concentration from a completely mixed aerobic reactor. This solution forms the basis for extensive analysis of the process behaviour. A comprehensive analysis is not required here; for those interested reference should be made to Ekama, van Haandel and Marais (1979) and van Haandel and Marais (1981).

3.1 Effluent Ammonia Concentration

Assume nitrification in a completely mixed reactor, under constant flow and load conditions (see Fig 5.2). A mass balance on the accumulation of nitrifier mass $M(\Delta X_n)$ is given by

$$M(\Delta X_n) = V_p\ \Delta X_n = [\mu_{nmT}.N_a/(K_{nT} + N_a)].X_n.V_p\ \Delta t$$

$$- b_{nT}.X_n.V_p.\Delta t - X_n.q.\Delta t$$

where

V_p = process volume (ℓ)

q = volumetric withdrawal rate of sludge *from the reactor* (ℓ/d)

Dividing by $V_p\ \Delta t$

$$\Delta X_n/\Delta_t = [\mu_{nmT}\ N_a/(K_{nT} + N_a)]X_n - b_{nT}\ X_n - X_n\ q/V_p$$

$$\text{Now } \frac{V_p\ X_n}{q\ X_n} = \frac{\text{Mass of nitrifier sludge in process}}{\text{Mass of nitrifier sludge wasted per day}} = \frac{V_p}{q} = R_s$$

where

R_s = sludge age (d) (see Eq 4.2).

Under constant flow and load, when steady state is achieved, $\Delta X/\Delta t = 0$ and solving for N_a yields,

$$N_a = \frac{K_{nT}\ (b_{nT} + 1/R_s)}{\mu_{nmT} - (b_{nT} + 1/R_s)} \qquad (5.13)$$

It is of interest to note that in Eq (5.13) the ammonia concentration (N_a) in the reactor (and effluent) is independent of the specific yield constant (Y_n) and the influent ammonia concentration (N_{ai}). Using the same nitrification kinetic constants as those in Fig 5.1 and taking $b_{nT} = 0{,}0$, a plot of Eq (5.13) with N_a versus sludge age R_s is given in Fig 5.2. Note that at long sludge ages N_a is very low and remains so until the sludge age is lowered to about 3,5 days below which, N_a increases rapidly until, in terms of this equation, N_a can exceed the influent concentration, N_{ai} - evidently the limit of application of the equation is when $N_a = N_{ai}$. Substituting N_{ai} for N_a in Eq (5.13) and solving for R_s gives the minimum sludge age, R_{sm}, below which theoretically, no nitrification can be achieved. This minimum sludge age varies slightly with the magnitude of N_{ai}, see Fig 5.2 - higher N_{ai} gives a *slightly* lower R_{sm}. Now the effective influent N_{ai} (see later) will rarely be less than about 20 mg/ℓ. Noting that $K_{nT} \cong 1$ mgN/ℓ, then K_{nT}/N_{ai} is negligibly small with respect to unity. Substituting zero for K_{nT}/N_{ai} in Eq (5.13) and solving for R_{sm}, yields

$$R_{sm} = 1/(\mu_{nmT} - b_{nT}) \qquad (5.14)$$

For practical application, Eq (5.14) adequately defines the minimum sludge age for all N_{ai} greater than about 5 mgN/ℓ.

The virtually constant value for R_{sm} (for the accepted values of μ_{nmT} and b_{nT}) and the rapid attainment of high nitrification efficiency at sludge ages slightly greater than R_{sm} causes that in a particular plant, as the sludge age is increased, once R_s exceeds R_{sm}, high efficiency of nitrification will be observed. Consequently, under steady state conditions one would expect a plant either not to nitrify, or, to nitrify with high efficiency depending on whether R_s is shorter or longer than R_{sm} respectively. This behaviour is well attested by observation on laboratory scale plants.

From the discussion above clearly the magnitudes of μ_{nmT} and b_{nT} affect R_{sm}; it is of importance, therefore, for practical application, to enquire into those factors that influence these constants and the nitrification phenomena in general.

4. FACTORS INFLUENCING NITRIFICATION

A number of factors affect the nitrification rate constants, efficiency of nitrification and the maximum sludge age. These are (1) Waste water source, (2) Temperature, (3) pH, (4) Unaerated zones, (5) Dissolved oxygen concentration, and (6) Cyclic flow and load.

4.1 Influent Source

The maximum specific growth rate constant μ_{nmT} has been observed to be specific to the source of the waste flow and, even then, to vary between different batches from the same source. This specificity is so marked that μ_{nmT} should be classified as a wastewater characteristic. The effect appears to be of an inhibitory nature due to some substance(s) in the wastewater. It is not toxicity because high efficiency of nitrification can be achieved even with a low μ_{nm} value if the sludge age is increased sufficiently. These inhibitory substances are more likely to be present in effluents having some industrial waste components and in general the higher this fraction the lower μ_{nmT} tends to be, but the specific waste fractions that cause the reduction of μ_{nmT} have not been clearly delineated. Taking the μ_{nmT} value at 20°C as the reference value, μ_{nm20} values have been

reported ranging from 0,33 to 0,65/d. These two limits will have a significant effect on the minimum sludge age: Two plants, having these respective μ_{nm20} values, will have R_{sm} values differing by hundred percent. Clearly due to the link between the waste flow and μ_{nmT}, the latter's value should always be estimated experimentally for optimal design. In the absence of such a measurement, a low value for μ_{nmT} necessarily will need to be selected which, for a particular waste flow, should the actual μ_{nm} be higher, will result in a non-optimal design. An experimental procedure to determine μ_{nm20} is given in Appendix 3.

With regard to b_{n20}, this value empirically is taken as constant for all waste flows, at b_{n20} = 0,04/d. Its effect is small so that there is no need to enquire closely into all the factors affecting it.

With regard to K_{nT} little information on effects of inhibitory agents is available; very likely K_{nT} will increase with inhibition.

4.2 Temperature

The μ_{nm} and K_n constants are sensitive to temperature with a high temperature coefficient (see Eq 5.15); semi-empirically b_{nT} is taken also to have temperature dependency at the same rate as that for heterotrophs (see Eq 5.16).

$$\mu_{nmT} = \mu_{nm20}\,(1{,}123)^{(T-20)} \qquad (5.15a)$$

$$K_{nT} = K_{n20}\,(1{,}123)^{(T-20)} \qquad (5.15b)$$

$$b_{nT} = b_{n20}\,(1{,}024)^{(T-20)} \qquad (5.16)$$

The effect of temperature on μ_{nmT} is particularly dramatic, for every 6 degC drop in temperature the μ_{nmT} value will halve which means that the minimum sludge age for nitrification will double. Design of plants for nitrification, therefore, should be based on the minimum expected process temperature. Note that the temperature sensitivity of K_{nT} does not affect the minimum sludge age, but it does affect the efficiency of nitrification - the higher the K_n the higher also the effluent ammonia at $R_s >> R_{sm}$ (See Section 4.3).

4.3 pH and Alkalinity

The specific growth rate of the nitrifiers μ_n is extremely sensitive to the pH of the culture medium. It seems that the activities* of both the hydrogen and hydroxyl ions, (H^+) and (OH^-) act inhibitorily when their respective concentrations increase unduly. This happens when the pH increases above 8,5 [increasing (OH^-)] or decreases below 7 [increasing (H^+)]; optimal nitrification rates are expected for $7 < pH < 8,5$ with sharp declines outside this range.

From Eq 5.4, μ_n is a function of both μ_{nm} and K_n. From an analysis of Eq (5.13) it was shown earlier that the minimum sludge age is dominated by the magnitude of μ_{nmT}; it is only very weakly influenced by K_{nT}. At $R_s >> R_{sm}$ however, the effluent ammonia concentration (N_a), although low, is relatively speaking, significantly higher for larger K_{nT} values: For example if K_{nT} increases by a factor of two, the effluent ammonia concentration will increase correspondingly by the same factor (see Eq 5.13). Consequently the value of K_{nT} is significant in so far as it controls the effluent ammonia concentration at $R_s >> R_{sm}$.

With regard to experimental estimates of μ_{nmT} and K_{nT}, a great amount of research has gone into tracing the effect pH has on μ_{nmT}. These investigations generally have not separated out the effects of μ_{nmT} and K_{nT} so that most data are in effect lumped parameter estimates of μ_{nmT}. Almost no information is available on the effect of pH on K_{nT}. The effect of pH on K_{nT} can be surmised from data obtained in a laboratory scale completely mixed reactor aerobic activated sludge investigation on a waste flow from Somerset West in the Cape Province. The plant was operated at 20°C over a range of sludge ages from 2 to 30 days. The response of the plant in terms of pH, filtered effluent TKN and nitrate plus nitrite is shown in Fig 5.3. Concomitant with nitrification the pH declined, stabilizing at about 4 when the sludge age exceeded 15 days. The TKN stabilized at

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* Equivalent to concentration.

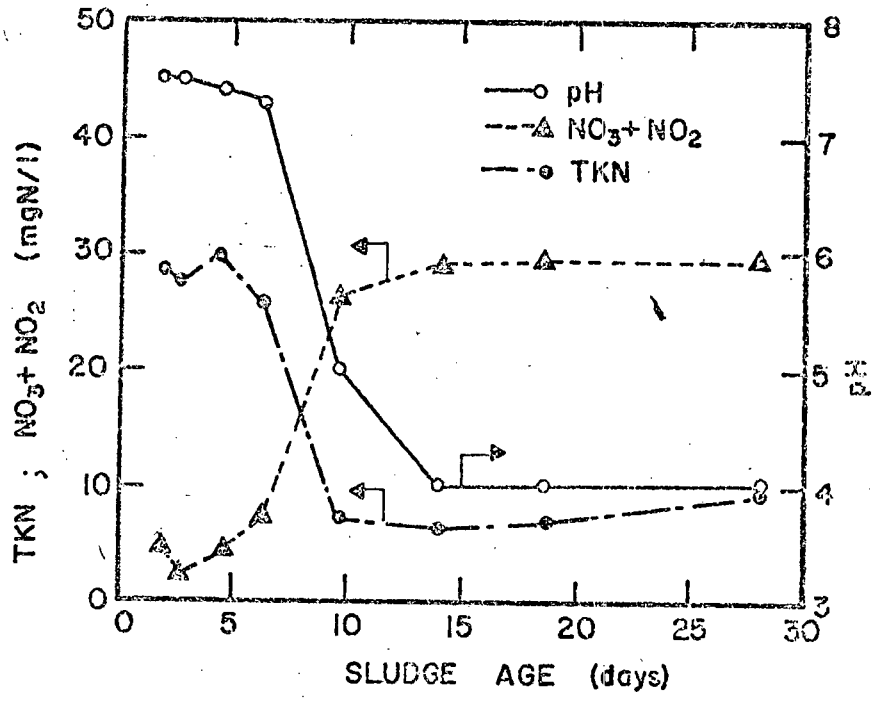

Fig 5.3 *Relationship between TKN and nitrate concentrations and pH with sludge age in an activated plant treating weakly buffered influent sewage from the Strand-Somerset West area, Cape.*

10 mgN/ℓ. Up to 10 days sludge age, the pH and nitrate concentration fluctuated in a see-saw fashion. The fact that stable nitrification was achieved only at 10 days sludge age when the pH was low, indicated that μ_{nmT} had decreased to a concomitantly low value. The fact that the effluent TKN (≅ ammonia) stabilized at the high value of 10 mg/ℓ indicated that K_{nT} had increased. On controlling the pH at 7,0 nitrification commenced at about 3 days sludge age and the effluent TKN (≅ ammonia) stabilized at about 4 mg/ℓ for R_s > 3 days. Evidently the pH and μ_{nmT} reacted interactively so that the minimum sludge age would fluctuate with the pH and achieve stability only at the long sludge age of 10 to 15 days. Evidently also the K_{nT} value is increased at low pH values. Due to the lack of information it is difficult to model quantitatively the effect of pH on μ_{nmT} and K_{nT}. The following analysis, based on various data sources and empirical assumptions on the behaviour, demonstrates the general expected trends even though the predicted values cannot be taken as quantitatively correct. Accepting that μ_{nm} remains constant for 7,2 < pH < 8,5 and decreases as the pH decreases below 7,2 (Downing *et al.* 1964, Loveless and Painter, 1968) this behaviour can be modelled as follows:

For 7,2 < pH < 8,5,

$$\mu_{nmpH} = \mu_{nm7,2} \qquad (5.17a)$$

For 5 < pH < 7,2,

$$\mu_{nmpH} = \mu_{nm7,2}\ \Phi_{ns}^{(pH-7,2)} \qquad (5.17b)$$

where

Φ_{ns} = pH sensitivity coefficient
≅ 2,35.

In Fig 5.4 the predictions, using Eq (5.17) are compared with experimental data on μ_{nm} collected by Malan and Gouws (1966). This comparison is illustrative only as it is not clear from the data of Malan and Gouws whether the effect of pH on K_n was taken into account when calculating μ_{nmpH}.

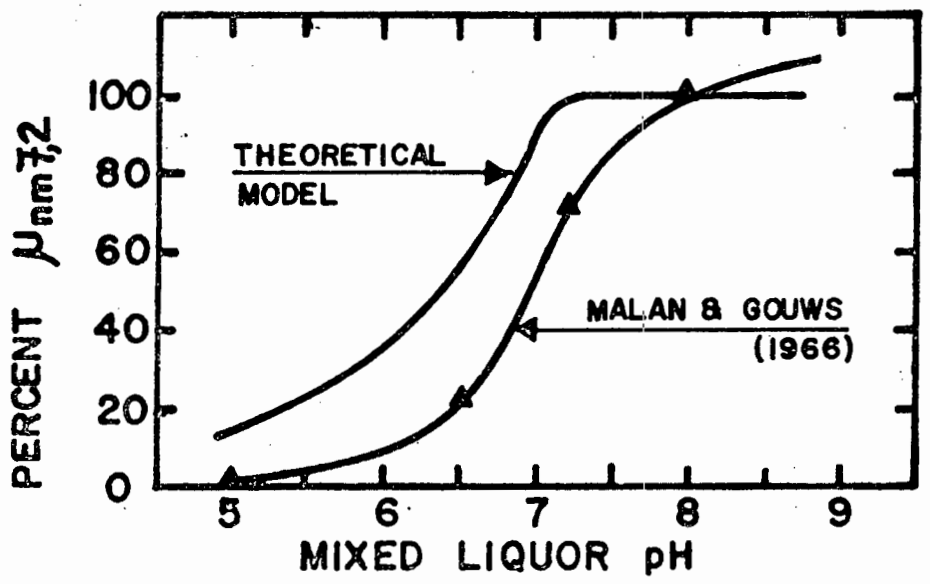

Fig 5.4 *Relationship between maximum specific growth rate for nitrosomonas, μ_{nm}, and mixed liquor pH. Experimental data after Malan and Gouws (1966)*

Changes in the value of K_n with pH are not at all documented in the literature. The best that can be done is to accept a dependency on pH and check the predictions against ammonia effluent concentrations reported at the different pH values. On this basis the following equations are suggested,

For $7,2 < pH < 8,5$

$$K_{npH} = K_{n7,2} \tag{5.18a}$$

For $5 < pH < 7,2$

$$K_{npH} = K_{n7,2}\ \Phi_{ns}^{(7,2-pH)} \tag{5.18b}$$

where

Φ_{ns} = pH sensitivity coefficient

$\cong 2,35.$

The overall effect of pH and temperature on μ_n can be modelled by substituting Eqs (5.15, 5.17 and 5.18) into Eq (5.4) i.e.

μ_{nTpH} = μ_n at temperature T°C and pH equal to pH.

$$\mu_{nTpH} = \frac{\mu_{nm20}(2,35)^{(pH\ -\ 7,2)}(1,123)^{(T-20)} \cdot N_a}{(K_{n20}(2,35)^{(7,2\ -\ pH)}(1,123)^{(T-20)} + N_a)} \tag{5.19}$$

where

μ_{nTpH} = specific growth rate at temperature T and pH = pH

μ_{nm} = maximum specific growth rate at temperature 20°C and pH = 7,2

K_n = saturation coefficient at temperature 20°C and pH = 7,2.

Although Eq (5.19) is qualitative in prediction only, it serves an important function in illustrating the adverse effects that temperature and pH can have on μ_n: A plot of μ_{nTpH} shown in Fig 5.5 for selected values of pH and temperature accepting $\mu_{nm20(7,2)}$ = 0,33/d and $K_{n20(7,2)}$ = 1,00 mgN/ℓ. Clearly low pH and low temperature can have significant effects on design.

In design the temperature effects have to be accepted as restrictions imposed by the environment. With regard to the effects of low pH, these may, or may not, occur depending on the Alkalinity of the influent. Low influent Alkalinity is likely to give rise to low pH in the purely aerobic activated sludge process. However it is possible to limit, or completely obviate, pH reduction by operating the plant as an anoxic-aerobic process. The reasons for this are as follows:

From the overall stoichiometric equations for nitrification (Eqs 1a and 1b), nitrification releases hydrogen ions which in turn decreases Alkalinity* of the mixed liquor. For every 1 mg (NH_4^+-N) that is nitrified 7,14 mg Alkalinity (as $CaCO_3$) is destroyed. Based on equilibrium chemistry of the carbonate system (Loewenthal and Marais 1977), equations linking the pH with Alkalinity for any partial pressure of carbon dioxide have been developed by van Haandel and Marais (1981). These relationships are shown plotted in Fig 5.6. When the Alkalinity falls below about 40 mg/ℓ as $CaCO_3$ then, irrespective of the partial pressure of carbon dioxide, the pH becomes unstable and tends to decrease to low values. Generally, if nitrification causes the Alkalinity to drop below about 40 mg/ℓ (as $CaCO_3$) problems associated with low pH very likely will arise in the plant, such as poor nitrification efficiency, tendency for developing bulking sludges, corrosive effluent, etc.

For any particular waste water the possible effect of pH can be readily assessed, as follows: Take the example of an influent having an Alkalinity of 200 mg/ℓ as $CaCO_3$; expected production of

*Alkalinity signifies the Total Alkalinity obtained by titrating the sample to an equivalent carbonic acid solution at pH approximately 4,3.

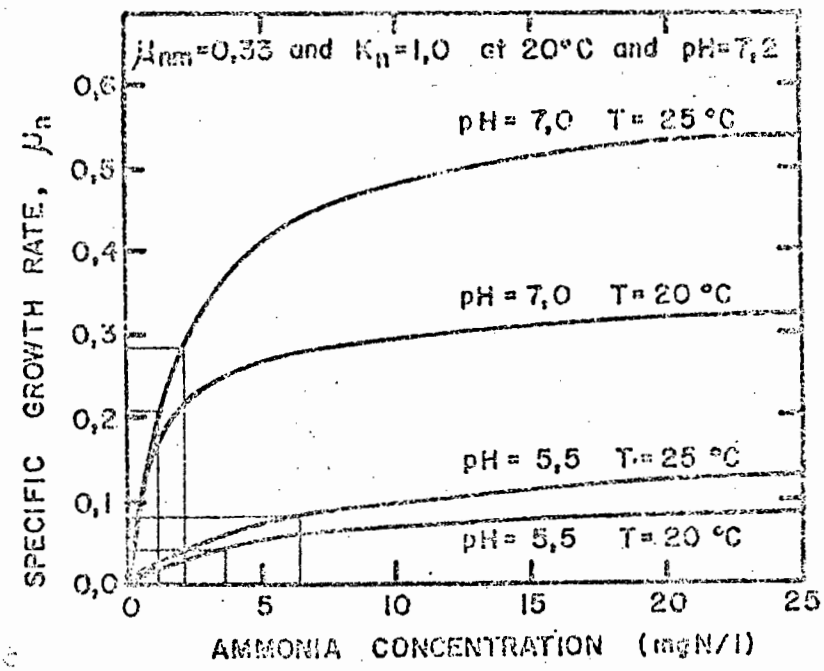

Fig 5.5 *Diagrammatic representation of Eq (5.19) - relationship describing the specific growth rate of* Nitrosomonas *for changes in temperature and mixed liquor pH*

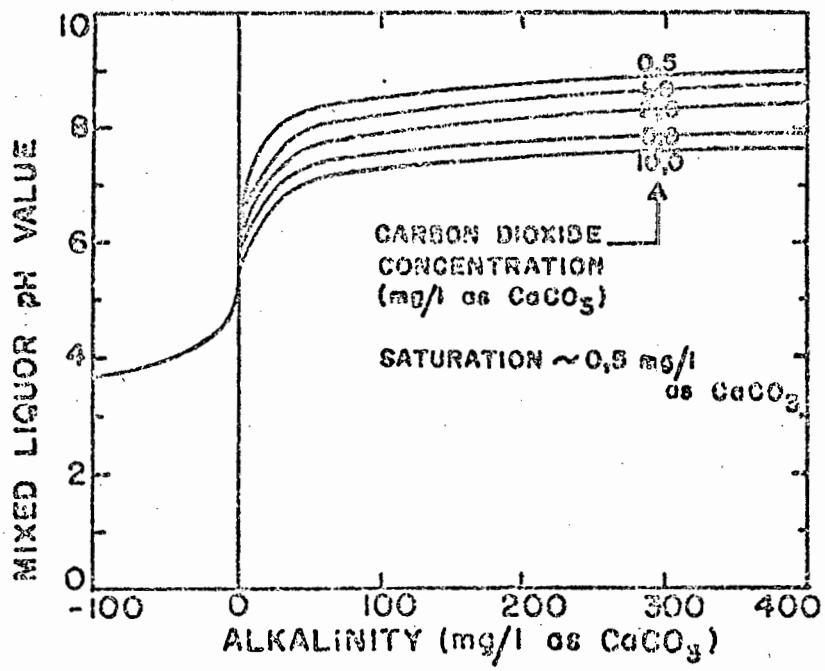

Fig 5.6 *Mixed liquor pH versus alkalinity for different concentrations of carbon dioxide.*

nitrate is 24 mgN/ℓ. The expected Alkalinity in the effluent will be (200 - 7,14.24) = 29 mg/ℓ as $CaCO_3$. From Fig 5.6, such an effluent is likely to have a pH < 7,0.

Waste waters having low Alkalinity are often encountered where the municipal supply is drawn from areas underlain with sandstone.

The abovementioned problems are to be expected in aerobic nitrifying plants treating municipal effluents of towns located in the coastal areas of South Africa, from Cape Town to, and including, Natal. The effluent from Somerset West mentioned earlier (see Fig 5.3) is a typical example. The only practical approach to treating such effluents is to create an anoxic zone in the process to denitrify some or all of the nitrate generated. In contrast to nitrification, denitrification takes up hydrogen ions which is equivalent to generating Alkalinity. By considering nitrate as electron acceptor, it can be shown that for every mg (NO_3-N) denitrified, there is an increase of 3,57 mg Alkalinity as $CaCO_3$. Hence incorporating denitrification in a nitrification process causes the net loss of Alkalinity to be reduced usually sufficiently to maintain the Alkalinity above 40 mg/ℓ and consequently the pH above 7.*

In the example above, where the Alkalinity in the process is expected to decline to 29 mg/ℓ as $CaCO_3$, if 25% of the nitrate could be denitrified the gain in Alkalinity would be (0,25.29.3,57) = 26 mg/ℓ as $CaCO_3$ and will result in an Alkalinity of (29 + 26) = 55 mg/ℓ as $CaCO_3$ in the process. In this event the pH should remain above 7. For low Alkalinity wastewaters it is imperative, therefore, that denitrification be built into nitrifying plants.

Incorporation of unaerated zones in the process influences the sludge age of the process at which nitrification takes place so that cognizance must be taken of the effect of an anoxic or unaerated zone in establishing the sludge age of a nitrifying-denitrifying plant.

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*Quantitative estimation of the denitrification that can be achieved in an anoxic-aerobic process is considered in Chapter 6.

4.4 Unaerated Zones

The effect of unaerated zones on nitrification can be readily formulated if the following assumptions are made:

(1) Nitrifiers, being obligate aerobes, can grow only in the aerobic zones of a process

(2) Endogenous mass loss of the nitrifiers occurs under both aerobic and unaerated conditions

(3) The concentration of nitrifiers in the unaerated and aerated zones is essentially equal.

With these assumptions, Ekama, van Haandel and Marais (1979) showed that if a fraction f_{xt} of the total sludge is unaerated, i.e. $(1-f_{xt})$ is aerated, the effluent ammonia is given by

$$N_a = \frac{K_{nT}\,(b_{nT} + 1/R_s)}{\mu_{nmT}\,(1-f_{xt}) - (b_{nT} + 1/R_s)} \qquad (5.20)$$

Equation (5.20) is identical in structure to Eq (5.13), if one views the effect of the unaerated mass (f_{xt}) as reducing the value of μ_{nmT} to $\mu_{nmT}\,(1-f_{xt})$.

Following the same reasoning as that preceding Eq (5.14) one can show that the minimum sludge age for nitrification R_{sm} in a process having an unaerated mass fraction, f_{xt}, is

$$R_{sm} = \frac{1}{\mu_{nmT}\,(1-f_{xt}) - b_{nT}} \qquad (5.21)$$

Alternatively, if R_s is specified the minimum aerobic sludge mass fraction $(1-f_{xm})$ that must be present for nitrification is found by substituting R_s for R_{sm} and f_{xm} for f_{xt} in Eq (5.21) and solving for $(1-f_{xm})$

$$(1-f_{xm}) = (b_{nT} + 1/R_s)/\mu_{nmT} \qquad (5.22)$$

or equivalently the maximum allowable unaerated sludge mass fraction

is given by solving for f_{xm} in Eq 5.22,

$$f_{xm} = 1 - (b_{nT} + 1/R_s)/\mu_{nmT} \qquad (5.23)^*$$

For a fixed sludge age, R_s, the design value for the minimum aerobic sludge mass fraction $(1-f_{xm})$ always should be significantly higher than that given by Eq (5.22), because nitrification becomes unstable when the aerated sludge mass fraction decreases to near the minimum value as given by Eq (5.22). Consequently to ensure *efficient* nitrification (>90%) the *minimum aerobic sludge mass fraction* $(1-f_{xm})$ must be increased by a factor of safety, S_f to give the *minimum design aerobic sludge mass fraction;* from Eq (5.22),

$$(1-f_{xm}) = S_f\ (b_{nT} + 1/R_s)/\mu_{nmT} \qquad (5.24a)$$

and the corresponding *maximum design unaerated sludge mass fraction*, from Eq (5.23) is

$$f_{xm} = 1 - S_f\ (b_{nT} + 1/R_s)/\mu_{nmT} \qquad (5.24b)$$

With the aid of the temperature dependency equations for nitrification (Eqs 5.15 and 5.16), a diagrammatic representation of Eq (5.24) is given in Fig 5.7 for $S_f = 1{,}25$ $\mu_{nm20} = 0{,}65$ and $0{,}33$/d at 14°C and 20°C. The two μ_{nm20} values are the approximate extremes of the range of μ_{nm20} values reported in the literature. The diagram shows that f_{xm} is very sensitive to the maximum specific

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*The usual approach for determining f_{xm} is based on the concept of "aerobic sludge age" i.e. equating the minimum sludge age for nitrification R_{sm} to the aerobic sludge age of the process R_{sa}. This leads to $f_{xm} = 1-1/\{R_s(\mu_{nmT}-b_{nT})\}$. This equation overestimates the maximum unaerated sludge mass f_{xm} at a particular sludge age because the approach ignores the endogenous mass loss of the nitrifiers in the unaerated zones. If the endogenous mass loss can be ignored in nitrification kinetics i.e. $b_n = 0{,}0$, then the two approaches are equivalent.

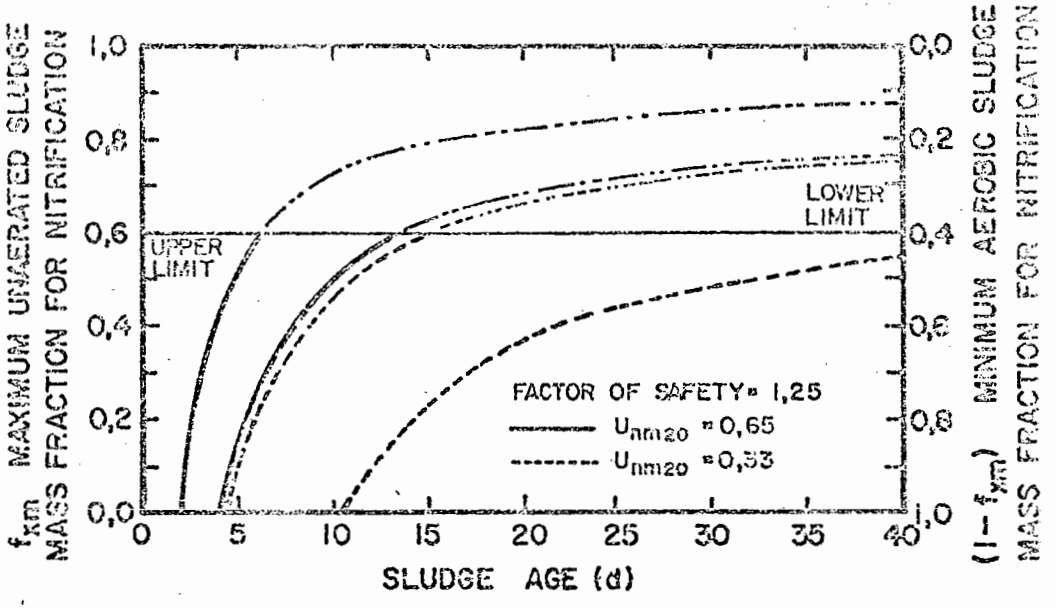

Fig 5.7 *Maximum allowable unaerated sludge mass fraction and minimum aerated sludge mass fraction required to sustain nitrification versus sludge age for different maximum specific growth rates of the nitrifiers at 20°C and 14°C and* S_f = 1,25.

growth rate of the nitrifiers (μ_{nmT}): unless a sufficiently large *aerobic* sludge mass fraction is provided (i.e. $1-f_{xm}$, see right hand of Fig 5.7), nitrification will not take place and consequently nitrogen removal by denitrification is not possible.

If one fixed minimum design aerobic sludge mass fraction, the sludge age can be determined by solving for $(1-f_{xm})$ Eq (5.24a). Knowing R_s the value of the effluent ammonia concentration (N_a) can be determined from Eq (5.20). By doing a number of solutions of this kind, at 14°C, it will become apparent that if S_f is selected at 1,25 or greater the effluent quality will have stability and range from 2 to 4 mg $(NH_3-N)/\ell$ depending on the other constants in the formulations. Accepting the sludge age as determined at 14°C, then at 20°C the value of S_f will be found to have increased significantly and the effluent ammonia to have decreased to 2 mg/ℓ or less. Consequently, for design the lower expected temperature should be selected to determine the sludge age and the aerobic mass fraction. If this is done, using S_f = 1,25, one can accept an effluent ammonia value of 2-4 mgN/ℓ at the lowest temperature and 1-3 mgN/ℓ at 20°C, that is, Eq (5.20) is bypassed by the approximation above, provided R_s at least equals 1,25 R_{sm}. This approximation is sufficient for design and will be the approach followed in the design example.

4.4.1 Maximum allowable unaerated mass fraction

The equations above allowed the maximum *design* unaerated sludge mass fraction to be determined for any selected sludge age Eq (5.24b). If one accepts S_f = 1,25 then f_{xm} or $(1-f_{xm})$ can be

plotted versus R_s for any selected μ_{nmT}. This is illustrated in Fig 5.7 where the design (f_{xm}) and ($1-f_{xm}$) values are plotted versus R_s for 20°C and 14°C for two selected μ_{nm20} reference values of 0,65 and 0,33 (b_{n20} was fixed at 0,04/d). Evidently from Fig 5.7, for μ_{nm20} = 0,65 the unaerated mass fraction at 14°C can be *approximately* 0,8 at sludge age of 30 days. Such a high unaerated mass fraction is the indicated one theoretically at R_s = 10 days or longer at 20°C. One may now ask: Is this mass fraction acceptable for design or are other constraints present that may limit the fraction to lower values? To answer this, two aspects appear to be pertinent:

(1) Experience with laboratory scale nitrification denitrification plants tends to support the opinion that at high unaerated mass fractions, the process is prone to bulking particularly at low temperatures. Processes at unaerated mass fractions of 0,5 or less show much less tendency in this regard.

(2) An upper limit to the unaerated mass fraction is evident from experimental work on the Ludzack-Ettinger process, and theoretical predictions using the general activated sludge model. Experimentally at 20°C with R_s = 20 days, if $f_{xm} > 0,70$, the mass of sludge generated is found to increase sharply. This observation is indicated also by theoretical simulation. Theoretically, this happens for $f_{xm} > 0,60$ at T = 14°C and R_s = 20 days. The reason is that for such high f_{xm}, the exposure of the sludge to aerobic conditions becomes insufficient to utilize the adsorbed and enmeshed particulate material. This leads to a decrease in active mass and oxygen demand and a build-up of enmeshed material, which causes a progressive decline in process activity because of the decline in active mass. When this happens, the process still *functions* in that the COD is removed from the wastewater, but the degradation of the COD is reduced; the process begins to assume the role of a contact reactor of a contact-stabilization process, i.e. a bio-flocculator with minimal degradation. This critical state occurs at lower f_{xm} as the temperature is decreased and the sludge age is reduced (Arkley and Marais, 1982).

From the discussion above it would appear that the unaerated mass fraction should not be allowed to increase above a certain upper limit, of about 50% but certainly not above 60%, as indicated in Fig 5.7.

In design of N and P removal plants the unaerated sludge mass fraction f_{xm} usually needs to be high i.e. ≧40%. If the μ_{nm20} value is low i.e. <0,40/d (which will be the usual case in design where insufficient information on the μ_{nm20} is available) the necessary high f_{xm} magnitudes will be obtained only at long sludge ages (see Fig 5.7). For example, if μ_{nm20} = 0,35/d, then with S_f = 1,3 at T_{min} = 14°C, for an f_{xm} = 0,45 (Eq 5.24b) gives a sludge age of 25 days and for f_{xm} = 0,55 a sludge age of 37 days. Long sludge ages require large process volumes - increasing R_s from 25 to 37 days increases the process volume by 40% (see Fig 4.3) whereas f_{xm} increased only 22%. Also, for the same P content in the sludge mass, the P removal is reduced as the sludge age increases because the mass of sludge wasted daily decreases as the sludge age increases (see Fig 4.4). Consequently, for low μ_{nm20} values, the increase in N and P removal that can be obtained by increasing the unaerated sludge mass fraction above 0,50 to 0,60 might not be economical due to the large process volumes this will require, and might even be counter productive insofar as it affects P removal. A sludge age of 35 days probably is near the limit of economic practicality which, for low μ_{nm14} = 0,16 values will limit the unaerated mass fraction to about 0,5. At higher μ_{nm14} values, the sludge ages allowing 50 percent unaerated mass fractions decrease significantly again indicating the advantages of determining experimentally the value of μ_{nm20} to check whether a higher value is acceptable.

4.5 Dissolved oxygen concentration

High dissolved oxygen concentrations, up to 33 mg/ℓ, do not appear to affect nitrification rates significantly. Low oxygen concentrations however do reduce the nitrification rate. Stenstrom and Poduska (1980) have suggested formulating this effect as follows:

$$\mu_{no} = \mu_{nmo} \frac{O}{K_o + O} \qquad (5.25)$$

where

O = oxygen concentration in bulk liquid (mg/ℓ)

K_o = half saturation constant (mgO/ℓ)

μ_{nmo} = maximum specific growth rate (/d)

μ_{no} = specific growth rate at DO mg/ℓ oxygen.

The value attributed to K_o has ranged from 0,3 to 2 mgO/ℓ, i.e. at DO values below K_o the growth rate will decline to less than half the rate where oxygen is present in adequate concentrations.

The wide range of K_o probably has arisen because the concentration of DO in the bulk liquid is not necessarily the same as inside the biological floc where the oxygen consumption takes place. Consequently the value will depend on the size of floc, mixing intensity and oxygen diffusion rate into the floc. Furthermore in a fullscale reactor the DO will vary over the reactor volume due to the discrete points of oxygen input (with mechanical aeration) and the impossibility of achieving instantaneous and complete mixing. For these reasons it is not really possible to establish a generally applicable minimum oxygen value - each reactor will have a value specific to the conditions prevailing in it. In nitrifying reactors with bubble aeration a popular DO lower limit, to ensure unimpeded nitrification, is 2 mgO/ℓ at the surface of the liquid.

Under cyclic flow and load conditions the difficulties of ensuring an oxygen supply matching the oxygen demand and a lower limit for the DO have been discussed previously (see Chapter 4, Section 11.3), Equalization of the load probably presents the best practical means to facil control of the oxygen level in the reactor. In the absence of equalization, mitigation of the adverse effects of low oxygen concentration during peak oxygen demand periods is by having sludge ages significantly longer than the minimum necessary for nitrification.

4.6 Cyclic Flow and Load

It is well attested experimentally that under cyclic flow and load conditions the nitrification efficiency of an activated sludge process decreases compared to that under steady state conditions. This behaviour is also apparent in simulation studies using the general activated sludge model. From the simulation studies, during the high flow and/or load period, even though the nitrifiers are operating at their maximum rate, it is not possible to oxidize all the ammonia available, and an increased ammonia concentration is discharged in the effluent. This in turn reduces the mass of nitrifiers formed in the process - equivalently the effect of cyclicity in flow and load is to reduce the aerobic sludge age. The adverse effect of the cyclicity becomes more marked as the fractional amplitude of the flow and load cycles increase, and, is ameliorated as the aerobic sludge age increases. Simulation studies of the cyclic effect have indicated that an approximate relationship can be established between the effluent ammonia concentration under steady state and that under cyclic conditions (see van Haandel and Marais 1981). However if the factor of safety on nitrification, S_f, is 1,25 or greater the cyclic effect is relatively small and for design usually can be neglected.

At the risk of being tedious, it should again be pointed out that if the value of μ_{nm} is selected higher than the actual value, even with a sludge of 1,25 to 1,35 times the theoretical minimum, the plant is likely to give rise to a fluctuating nitrate effluent with reduced mean efficiency in nitrification. Hence a conservative estimate of μ_{nm} is essential for a safe design.

Under cyclic flow and load conditions, it is necessary to know the value of both the specific yield coefficient of the *Nitrosomonas*, Y_n, the maximum specific growth rate constant μ_{nmT} and the half saturation constant, K_n; in contrast, only μ_{nmT} and K_n are necessary in steady state calculations. The values of these constants have been determined by a variety of methods but the constants have a conjoined effect that may cause that in a particular method of evaluation leads

to different sets of values. For practical purposes it is not possible to obtain a complete set of values so that one approach is to accept the value of one constant and in any particular experimental evaluation determine the other constants from the experimental data using this value. The estimates for Y_n and K_n accepted in this monograph are listed in Table 5.1; experimental μ_{nm} determination, therefore, is relative to the value of Y_n and K_n listed.

5. DESIGN CONSIDERATIONS

5.1 Fate of the Influent TKN

The various fractions of the influent TKN have been described in Chapter 2. Of these the following are of importance to our discussion; (1) free and saline ammonia concentration (N_{ai}), (2) biodegradable organic nitrogen (N_{oi}) and the soluble unbiodegradable organic nitrogen (N_{ui}).

The bioldegradable organic nitrogen is decomposed in the process by heterotrophic action to free and saline ammonia. Furthermore, on death of the organisms, by endogenous mass loss, the nitrogen released is in the organic bound form and the biodegradable fraction also is broken down to free and saline ammonia. These two sources of

Table 5.1 Kinetic constants for *Nitrosomonas* accepted in this monograph.

Constant	Symbol	Value at 20°C	Temperature Coefficient	Eq No.
Specific yield coefficient	Y_n	0,10	1,000	-
Endogenous respiration rate	b_n	0,04	1,029	5.16
Half saturation coefficient	K_n^*	1,00	1,123	5.15b

*Note that K_n increases with increase in temperature.

free and saline ammonia together with that in the influent are utilized by the organism mass first for the formation of new organisms and the balance for generation of nitrate, if the conditions are favourable.

The 'exact' formulations describing the interactions between the free and saline ammonia and the organic bound nitrogen are complex and can be developed effectively (at present) only in terms of the growth-death-regeneration model of Dold, Ekama and Marais (1981).* However under steady state conditions the kinetics simplify and the formulations reduce to describing net effects. These can be developed readily in terms of the synthesis - endogenous respiration approach already used to develop the steady state equations for carbonaceous material degradation, in Chapter 4. For design there is even a further simplification possible: In nitrification systems if, for example, the constraints are put on the system that the minimum design sludge age must be at least 1,25 to 1,35 times the theoretical minimum to initiate nitrification, and, that the pH remains above 7, some of the steady state kinetic equations predict effluent concentrations that fall within a narrow band of values, sufficiently narrow that one can accept the effluent parameter virtually as constant.** Below we shall set down some of these steady state equations of importance in developing design procedures, indicate simple approximation adequate for design and derive some general response graphs.

In the design of those aspects of a process effecting nitrification, basically the following information is needed, (1) effluent TKN concentration, and (2) effluent nitrate concentration.

5.1.1 Effluent TKN

The effluent TKN will consist of free and saline ammonia (N_a), biodegradable soluble TKN (N_o), unbiodegradable soluble TKN (N_u) and TKN in the effluent volatile solids. Equations for the fractions are set out below:

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*A more elaborate discussion is available by van Haandel and Marais (1981).

**The same approach also applied in the design equations for carbonaceous material degradation that, provided R_S > 3 days usually one can accept the filtered *biodegradable* COD in the influent as zero (see Chapter 4, Section 3.4).

(1) Free and saline ammonia (N_a):

N_a is given by Eq (5.20), i.e.

$$N_a = \frac{K_{nT}\,(b_{nT} + 1/R_s)}{\mu_{nmT}\,(1-f_{xt}) - (b_{nT} + 1/R_s)} \qquad (5.20)$$

Note that N_a is independent of the influent ammonia concentration. Note also that the equation applies only if the sludge age $R_s > R_{sm}$, however this condition always should be satisfied in design.

(2) Biodegradable organic nitrogen concentration (N_o)

The biodegradable organic nitrogen is broken down to free and saline ammonia by heterotrophic organisms. Although a complex reaction, involving a feedback of this nitrogen form from death of the organisms, the prediction simulated by the general model indicated that the following equation, in terms of the influent biodegradable organic nitrogen concentration, is adequate

$$N_o = \frac{N_{oi}}{1 + K_r\, X_a\, R_{hn}} \qquad (5.26)$$

where

N_{oi} = influent biodegradable organic nitrogen mg(TKN-N)/ℓ. Its value is given by Eq (2.14).

K_r = kinetic constant for degradation of N_o. Its value and temperature dependency is given in Table 5.3 below.

X_a = active mass concentration in aerobic reactor.

R_{hn} = nominal hydraulic retention time in process.

(3) Soluble unbiodegradable organic nitrogen (N_u)

$$N_u = N_{ui} \qquad (5.27)$$

where

N_{ui} = soluble unbiodegradable organic nitrogen, mg(TKN-N)/ℓ. Its value is given by Eq (2.12).

All these effluent fractions are soluble; consequently the total soluble TKN in the effluent (N_t) is given by the sum of these, i.e.

$$N_t = N_a + N_o + N_u \quad \text{(filtered } N_t\text{)} \tag{5.28a}$$

The experimental value of N_t will be given by the TKN of the *filtered* effluent sample. If the sample is not filtered the theoretical TKN of the effluent will be greater by the concentration of TKN in the volatile solids, i.e.

$$N_{tv} = N_a + N_o + N_u + f_n.X_{vf} \quad \text{(unfiltered } N_t\text{)} \tag{5.28b}$$

where

X_{vf} = effluent volatile solid concentration (mgVSS/ℓ)

f_n = fraction of TKN in VSS $\cong$ 0,1 mg(TKN-N)/mgVSS.

5.3 Nitrification Capacity

The concentration of nitrate generated in the system (N_c) is given by the TKN in the influent (N_{ti}) less the soluble TKN in effluent (N_t) less the concentration of total influent TKN incorporated in the net sludge generated each day (N_s) i.e.

$$N_c = N_{ti} - N_t - N_s \tag{5.29}$$

The value of N_s is determined from the mass of nitrogen incorporated in the volatile solids per day. It is given by f_n times the mass of volatile solids wasted per day (MX_v/R_s), divided by the mean daily flow, i.e.

$$N_s = \frac{f_n.M(X_v)}{R_s.Q} \quad \text{(see Chapter 4, Section 9).}$$

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*This equation presumes that no nitrate is present in the influent and this is true, virtually always, for municipal flows.

where

$M(X_v)$ is given by Eq (4.13).

Note that $M(X_v)$ does not include the volatile mass of nitrifiers as the masses of these, we have stated previously, are negligible.

In Eq (5.29), N_c defines the *nitrification capacity* of the process. A formal definition of nitrification capacity (N_c) is the mass of nitrate produced per unit volume of flow, i.e. $mg(NO_3\text{-}N)/\ell$ of flow.

Equation (5.29) shows that the nitrification capacity (N_c) is the difference between the influent TKN concentration (N_{ti}) and the sum of the effluent TKN concentration (N_t) and the nitrogen required for sludge production (N_s). The effluent TKN concentration (N_t) depends on the efficiency of nitrification. In calculations, with maximum unaerated sludge mass fraction (f_{xm}), (for a selected sludge age), if the factor of safety (S_f) is selected greater than 1,25 to 1,35 at the *lowest expected temperature* (T_{min}), the efficiency of nitrification always will be high (>90%) and N_t generally will be less than 3 to 4 mgN/ℓ. Also, with $S_f \geq 1{,}25$ at T_{min}, N_t will be virtually independent of both the process configuration and the subdivision of the sludge mass into aerated and unaerated fractions. *Consequently, for design N_t usually need not be calculated explicitly from Eqs (5.20, 5.26 to 5.28), but can be taken to be approximately 3 to 4 mgN/ℓ* provided that there is reasonable assurance that the actual μ_{nm20} value will not be less than the value accepted for design and that there is sufficient aeration capacity so that nitrification is not inhibited by an insufficient oxygen supply. Accepting the calculated f_{xm} and selected sludge age (R_s) at the lower temperature, then at higher temperatures the nitrification efficiency and the factor of safety (S_f) both will increase so that at summer temperatures (T_{max}), N_t will be lower, approximately 2 mgN/ℓ.

Dividing Eq (5.29) by the total influent COD concentration (S_{ti}) yields the nitrification capacity per mgCOD applied to the biological process, N_c/S_{ti},

$$N_c/S_{ti} = N_{ti}/S_{ti} - N_s/S_{ti} - N_t/S_{ti} \qquad (5.30)$$

where

N_c/S_{ti} = nitrification capacity per mgCOD applied to the process (mgN/mgCOD)

N_{ti}/S_{ti} = TKN/COD ratio of the wastewater

N_s/S_{ti} = nitrogen required for sludge production per mgCOD applied (see Eq 4.23).

In Eq (5.30) the nitrification capacity/COD ratio (N_c/S_{ti}) of a process can be estimated approximately by evaluating each of the terms in the RHS of the equation as follows:

N_t/S_{ti} : Provided the constraint for efficient nitrification is satisfied at the lowest temperature (T_{min}) the TKN in the effluent (N_t) can be assumed at T_{min} to be about 4 mgN/ℓ i.e. N_t/S_{ti} will range from 0,005 to 0,01 for S_{ti} ranging from 800 to 400 respectively. At T_{max}, $N_t \cong 2$ mgN/ℓ.

N_s/S_{ti} : This ratio gives the TKN concentration in the influent abstracted for sludge production. Its value will depend on whether settled or raw waste water is being treated, and the sludge age. The ratio, N_s/S_{ti}, for this purpose can be read from Fig 4.5, or calculated from Eq (4.23).

N_{ti}/S_{ti} : This value is obtained by measurement of the TKN and COD of the influent and can range from 0,07 for unsettled municipal waste flows to 0,12 for settled flows.

A graphical exposition of the relative importance of these three ratios on N_c/S_{ti} is obtained by plotting N_c/S_{ti} versus sludge age for selected influent TKN/COD (N_{ti}/S_{ti}) ratios ranging from 0,07 to 0,09 for raw waste water and 0,09 to 0,11 for settled waste water. The N_c/S_{ti} values were found from Fig 4.5 (or Eq 4.23) and the N_t/S_{ti} values selected constant at 0,007 (this is for S_{ti} of approximately 600 mgCOD/ℓ). The plots for 14°C and 20°C are shown in Figs (5.8a and 5.8b) respectively. Also shown plotted on the diagrams are the

minimum sludge ages for unaerated mass fractions of 0,0, 0,2, 0,4 and 0,5, at a selected μ_{nm20} value of 0,4. For any particular unaerated mass fraction the plotted values of N_c/S_{ti} are valid only at sludge ages greater than the corresponding minimum sludge age. These plots allow one to assess the effects of the three ratios and temperature versus sludge age.

Considering the effects of temperature, to obtain complete nitrification at 14°C (for a selected f_{xm}), the sludge age required is more than double that at 20°C. The corresponding nitrification capacities per influent COD at 14°C show a marginal reduction to those at 20°C (because the sludge production at 14°C is slightly higher than at 20°C).

Considering the effect of sludge age for a selected N_{ti}/S_{ti} value, the N_c/S_{ti} increases as the sludge age increases because the nitrogen needed for sludge production decreases with sludge age and thus becomes available for nitrification. However the increase is marginal for R_s > 10 days.

Considering the influent TKN/COD ratio (N_{ti}/S_{ti}) evidently for both settled and unsettled waste water, at any selected sludge age, N_c/S_{ti} is very sensitive to the N_{ti}/S_{ti} value; an increase of 0,1 in N_{ti}/S_{ti} causes an increase of about 0,1 in N_c/S_{ti} (0,1 mgN/mgCOD). For the same N_{ti}/S_{ti} ratio for raw or settled waste water [compare TKN/COD ratio of 0,09 in Figs (5.8a and b)], N_c/S_{ti} for unsettled is less than for settled waste water because more volatile solids are produced per unit COD load from unsettled than by settled waste water; however leaving aside this point of difference, the increase in nitrate produced per influent COD will, when the influent TKN/COD ratio increases, increase the difficulties, or, make it impossible, to obtain complete denitrification. This will become clear when denitrification is considered in Chapter 6. As primary settling increases the influent TKN/COD ratio, difficulties in obtaining adequate denitrification are always greater with settled than unsettled waste water; however, because primary settling removes COD, then for the same flow, the mass of volatile solids and the oxygen demand in the

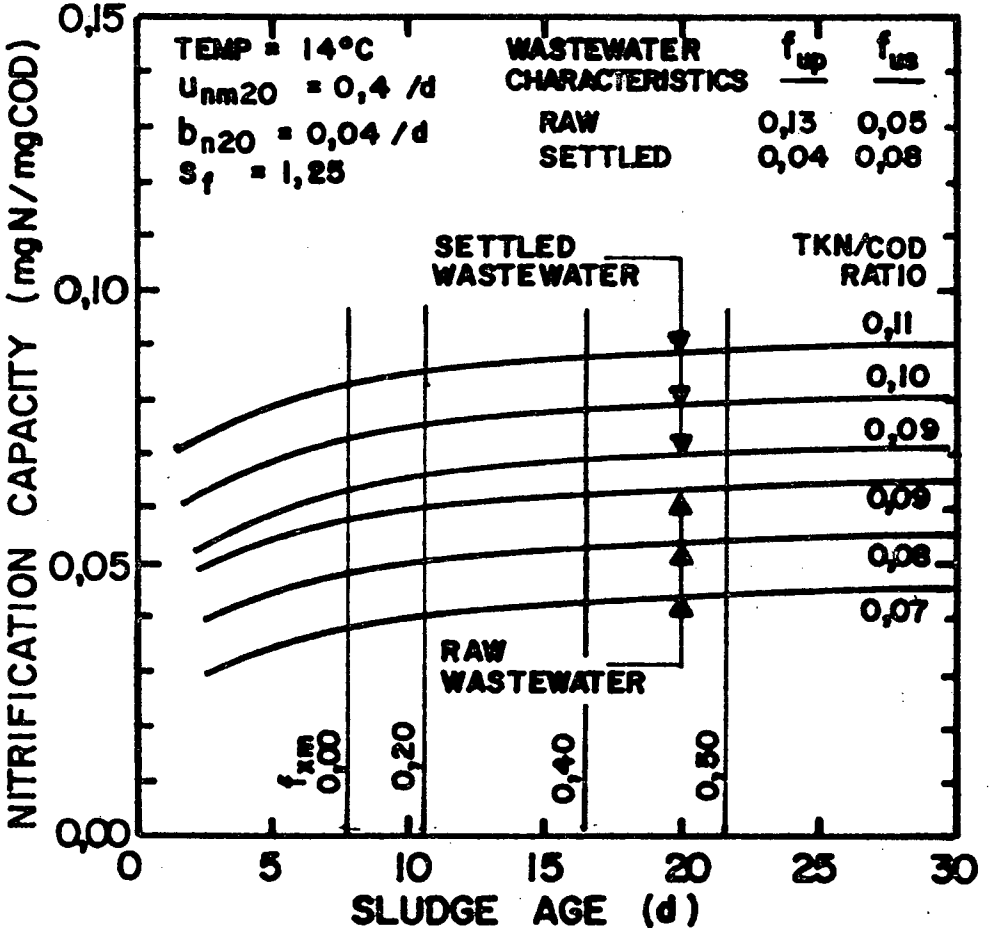

Fig 5.8a

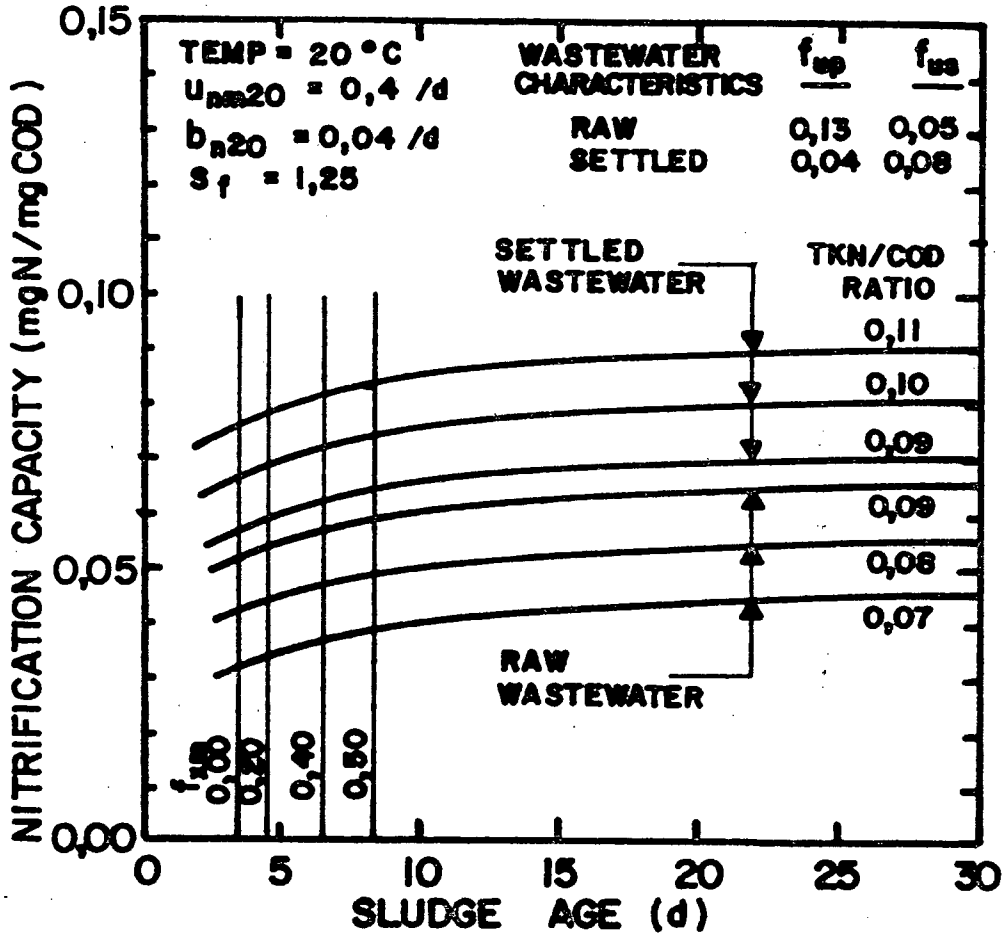

Fig 5.8b

Fig 5.8 *Nitrification capacity per mg COD applied versus sludge age for different influent TKN/COD ratios at 14°C (Fig 5.8a) and 20°C(5.8b). Also shown are the minimum sludge ages required to obtain complete nitrification at different unaerated sludge mass fractions for* μ_{nm20} = 0,40/d

biological process will be lower for settled than for raw wastewater thereby giving rise to savings in plant volume and oxygenation costs.

6. DESIGN EXAMPLE

Design of a nitrification process without denitrification will be considered. When denitrification is required constraints additional to those imposed by nitrification must be applied and these cannot be incorporated in the design until the theory of denitrification is dealt with.

For the purpose of constructive comparison the nitrifying activated sludge plant will be designed for the same waste flows and characteristics as that accepted for the design of a process for carbonaceous material removal (see Chapter 4, Section 12). The wastewater characteristics, for raw and settled wastewaters are listed in Table 4.3 and the additional characteristics needed for nitrification are listed in Table 5.2.

6.1 Effect of Nitrification on Mixed Liquor pH

An important initial consideration is the possible effect of mixed liquor pH on the μ_{nm20} value. In Section 4.3 above it was stated that nitrification consumes alkalinity - 7,14 mg/ℓ as $CaCO_3$ for every 1 mgN/ℓ ammonia converted to nitrate - and if there is insufficient alkalinity in the influent, the mixed liquor pH is depressed below 7,0 causing a reduction in the μ_{nm20} value (see Eq 5.17).

The influent TKN/COD ratio of the raw wastewater is 0,08 mgN/mgCOD (see Tables 4.3 and 5.2). With a relatively low μ_{nm20} value of 0,36/d, the sludge age needs to be 10 days or longer to ensure nitrification (S_f = 1,3) at a minimum temperature of 14°C in a purely aerobic process (f_{xm} = 0,0) (see Eq 5.24). At this sludge age the nitrification capacity is about 0,05 mgN/mgCOD for a TKN/COD ratio of 0,08 mgN/mgCOD, (see Fig 5.8a). Hence the nitrate concentration produced (per ℓ influent) should be about = 0,05.600 = 30 mgN/ℓ. This will cause an alkalinity reduction of 7,14.30 = 214 mg/ℓ as $CaCO_3$. Because the influent alkalinity is only 200 mg/ℓ as $CaCO_3$, the mixed liquor alkalinity will drop below 40 mg/ℓ as $CaCO_3$ causing the mixed

Table 5.2 Raw and settled wastewater characteristics for nitrification (see also Tables 4.3 and 6.1)

Parameter	Symbol	Value		Units
		Raw	Settled	
Influent TKN concentration	N_{ti}	48	41	mg N/ℓ
Influent TKN/COD ratio	–	0,080	0,114	mg N/mg COD
Ammonia fraction of TKN	f_{na}	0,75*	0,83*	mg N/mg N
Unbio. soluble organic N	f_{nu}	0,03*	0,04*	mg N/mg N
Nitrogen content of volatile solids in influent	f_n	0,10	0,10	mg N/mg VSS
pH of wastewater	-	7,5	7,5	-
Total alkalinity	alk	200	200	mg/ℓ as $CaCO_3$
Maximum specific growth rate of nitrifiers	μ_{nm20}	0,36	0,36	/d.
Influent flow	Q	13,3	13,3	Mℓ/d

liquor pH value to drop below 7 (see Fig 5.6). The low mixed liquor pH value will cause unstable and incomplete nitrification (see Section 4.3 above) and produce an aggressive water (which over a few years can cause considerable damage to the concrete surfaces of the treatment works) and can be the cause of bulking sludges and high solids content in the settling tank effluent due to denitrification action in the secondary settling tank.

The simple approximate calculation above, therefore, can make the designer aware, at an early stage, of possible adverse consequences to be expected from a proposed design. In the instance

*See Chapter 3, Section 8. Note that settled wastewater characteristics must be selected so that they are consistent with primary sedimentation tank behaviour and the raw wastewater characteristics.

above the designer should give consideration to a nitrification-denitrification process, to recover some of the alkalinity loss due to nitrification, thereby to maintain the pH, reduce the possibility of bulking and eliminate (usually) rising sludge problems in the settling tank. (See Chapter 6, Section 1.4). In general a high TKN/COD ratio coupled with low alkalinity in the influent are reliable indicators warning of problems to be expected in aerobic nitrifying processes.

6.2 Minimum Sludge Age for Nitrification

For the purposes of demonstrating nitrification under purely aerobic conditions, it will be accepted that the influent Alkalinity is sufficiently high to maintain an effluent Alkalinity above 40 mg/ℓ as $CaCO_3$. Hence no adjustment to μ_{nm20} and K_{n20} for pH need to be made as the pH is assumed to remain above 7,2. The adjustment of the kinetic constants of nitrification for temperature is given in Table 5.3.

For a completely aerobic process i.e. $f_{xm} = 0$, with $\mu_{nm20} =$ 0,36/d and $S_f = 1,3$, the minimum sludge age for nitrification (R_{sm})

Table 5.3 Adjustment of kinetic constants of nitrification for temperature.

Constant	Symbol	20°C	θ	14°C	22°C	Eq.No.
Max.specific growth rate	μ_{nm20}	0,36	1,123	0,180	0,454	5.15a
Saturation coefficient	K_{n20}	1,0	1,123	0,50	1,26	5.15b
Endogenous respiration rate	b_{n20}	0,04	1,029	0,034	0,042	5.16
Organic N conversion rate	K_r	0,015	1,029	0,013	0,016	5.31

is found from Eq (5.24) i.e.

$$R_{sm} = S_f/(\mu_{nmT} - b_{nT})$$

= 3,2 days at 22°C (2,5 days with S_f = 0,0)

= 8,9 days at 14°C (7,5 days with S_f = 0,0)

Clearly, to ensure nitrification throughout the year for the relatively low μ_{nm20} value of 0,36/d, the sludge age of a purely aerobic process should be about 10 to 12 days.

6.3 Raw Wastewater

The influent TKN concentration of the raw wastewater is 48 mgN/ℓ (see Table 5.2 for wastewater characteristics). Accepting an ammonia fraction of the influent TKN (f_{na}) of 0,75* and an unbiodegradable soluble organic nitrogen fraction (f_{nu}) of 0,03* for the raw sewage (from Table 5.2), gives the influent ammonia concentration (N_{ai}) (from Eq 2.11) as

$$N_{ai} = 0,75.48 = 36 \text{ mgN}/\ell$$

and the unbiodegradable soluble organic nitrogen concentration (N_{ui}), (from Eq 2.12) as

$$N_{ui} = 0,03.48 = 1,50 \text{ mgN}/\ell.$$

Accepting the nitrogen content of the volatile solids in the influent (f_n) as 0,10 mgN/mgVSS (see Table 5.2), then (from Eq 2.13) the nitrogen concentration associated with the unbiodegradable particulate COD (N_{pi}) is

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*The actual choice of these values makes relatively little difference to the final results of the nitrification calculations: in the case of the former (f_{na}), most of the organic nitrogen is converted to ammonia in the process and in the case of the latter (f_{nu}), this value merely increases the effluent TKN concentration by a fixed value.

$N_{pi} = 0,10\ (0,13.600)/1,48 = 5,3\ mgN/\ell.$

Hence (from Eq 2.14), the biodegradable organic nitrogen concentration in the influent which can be converted to ammonia (N_{oi}) is

$N_{oi} = 48\ (1 - 0,75 - 0,03) - 5,3 = 5,3\ mgN/\ell.$

6.4 Settled Wastewater

Following the above procedure for settled wastewater, i.e. $f_{na} = 0,83$, $f_{nu} = 0,04$ (see Table 5.2) yields the following:

$N_{ti} = 41,0 \qquad = 41,0\ mgN/\ell$

$N_{ai} = 0,83.41,0 \qquad = 34,0\ mgN/\ell$

$N_{ui} = 0,04.41,6 \qquad = 1,50\ mgN/\ell$

$N_{pi} = 0,10\ (0,04.360)/1,48 \qquad = 1,0\ mgN/\ell$

$N_{oi} = 41,0 - 34,0 - 1,5 - 1,0 = 4,5\ mgN/\ell$

6.5 Nitrification Process Behaviour

For any sludge age longer than about 2 days the effluent biodegradable organic nitrogen concentration (N_{oe}) is given (from Eq 5.26)

$$N^*_{oe} = N_{oi}/(1 + K_{rT}X_aR_{hn}) \qquad (mgN/\ell)$$

where from Eq (4.9a), $R_{hn}X_a = M(X_a)/Q$. Hence

$$N_{oe} = N_{oi}/(1 + K_{rT}M(X_a)/Q) \qquad (mgN/\ell) \qquad (5.31)$$

From Eq (5.27), the unbiodegradable organic nitrogen in the effluent is

$$N_{ue} = N_{ui} = 1,50\ mgN/\ell \text{ for raw and settled wastewater} \qquad (5.32)$$

---

*The subscript e used here and later refers to the effluent. However, $N_o = N_{oe}$, $N_a = N_{ae}$, etc.

The nitrogen required for sludge production (N_s) is given by Eq (4.23) i.e.

$$N_s = f_n \left\{\frac{(1 - f_{us} - f_{up})Y_h}{(1 + b_{hT}R_s)} (1 + fb_{hT}R_s) + \frac{f_{up}}{f_{cv}}\right\} S_{ti} \qquad (5.33)$$

The influent TKN concentration available for nitrification (N'_{ti}) is the difference between the total TKN concentration in the influent (N_{ti}) and that required for sludge production (N_s) (from Eq 5.19)

$$N'_{ti} = N_{ti} - N_s \qquad (5.34)$$

If the sludge age of the process is longer than the minimum required for nitrification ($R_s > R_{sm}$ for $S_f = 1{,}25$, Eq (5.24a) with $f_{xm} = 0$, the TKN concentration available for nitrification will be partially or almost wholly nitrified to nitrate and the effluent nitrate concentration (N_{ne}) is the difference between the nitrogen available for nitrification (N'_{ti}, Eq 5.34) and the effluent TKN concentration (N_{te}). If $R_s < R_{sm}$, no nitrification takes place; the effluent nitrate concentration (N_{ne}) is zero and the effluent ammonia concentration (N_{ae}) is equal to the nitrogen available for nitrification (N'_{ti}, Eq 5.34) minus the sum of the unbiodegradable and biodegradable TKN concentrations in the effluent ($N_{ue} + N_{oe}$). For both $R_s < R_{sm}$ and $R_s > R_{sm}$, the effluent TKN concentration (N_{te}) is the sum of effluent unbiodegradable and biodegradable organic nitrogen concentrations (N_{ue} and N_{oe} respectively) and the effluent ammonia concentration (N_{ae}).

For $R_s > R_{sm}$:

From Eq (5.13), the effluent ammonia concentration is given by

$$N_{ae} = K_{nT}(b_{nT} + 1/R_s)/\{\mu_{nmT} - (b_{nT} + 1/R_s)\} \qquad (5.35a)$$

Hence the effluent TKN concentration (N_{te}) is

$$N_{te} = N_{ae} + N_{oe} + N_{ue} \quad (mgN/\ell) \tag{5.36a}$$

and the effluent nitrate concentration (N_{ne}) is

$$N_{ne} = N'_{ti} - N_{te} \quad (mgN/\ell)$$

$$= N_{ti} - N_s - N_{te} \quad \text{(from Eq 5.34)} \tag{5.37a}$$

Analogous to the concentration of active heterotrophic organisms (see Eq 4.10), the nitrifier organism mass is given by

$$M(X_n) = M(N_{ne})\ Y_n R_s/(1 + b_{nT} R_s) \quad (mgVSS) \tag{5.38a}$$

where

$M(N_{ne})$ = mass of nitrate generated per day

$= Q.N_{ne}$

where N_{ne} is given by Eq (5.37a).

The oxygen demand for nitrification is simply 4,57 mgO/mgN times the mass of nitrate produced per day, i.e.

$$M(O_n) = 4{,}57\ M(N_{ne}) \quad (mgO/d) \tag{5.39a}$$

$R_s < R_{sm}$:

For $R_s < R_{sm}$, no nitrification takes place. Hence the effluent nitrate concentration is zero i.e.

$$N_{ne} = 0{,}00 \quad (mgN/\ell) \tag{5.37b}$$

The effluent ammonia concentration is

$$N_{ae} = N'_{ti} - N_{oe} - N_{ue} \quad (mgN/\ell)$$

$$= N_{ti} - N_s - N_{oe} - N_{ue} \quad \text{(from Eq 5.34)} \tag{5.35b}$$

The effluent TKN concentration is

$$N_{te} = N_{ae} + N_{ue} + N_{oe} \qquad (5.36b)$$

The nitrifier sludge mass and the nitrification oxygen demand are zero, i.e.

$$M(X_n) = 0,0 \qquad \text{(mgVSS)} \qquad (5.38b)$$

$$M(O_n) = 0,0 \qquad \text{(mgO/d)} \qquad (5.39b)$$

Substituting the respective influent nitrogen concentrations for raw and settled wastewaters and the values of the kinetic constants at 14°C into Eqs (5.31 to 5.39) and plotting the results at different sludge ages yields Fig 5.9. In Fig 5.9a, the different concentrations of nitrogen in the process versus sludge age for raw and settled wastewater at 14°C are shown. In Fig 5.9b the nitrifier sludge mass and nitrification oxygen demand for raw and settled wastewater at 14°C are shown. Also shown in Fig 5.9b are the carbonaceous and total oxygen demands for raw and settled wastewater at 14°C. The calculations were repeated for 22°C and are shown in Fig 5.10a and b.

Figures 5.9 and 5.10 show that once the sludge age is approximately 25 percent longer than the minimum required for nitrification, nitrification is complete and comparing the results for raw and settled wastewater, there is little difference between the nitrification oxygen demand and the concentrations of ammonia, nitrate and TKN in the effluent. The reasons for this similar behaviour are (1) the primary settling tank removes only a small fraction of the influent nitrogen* and (2) settled wastewater results in lower sludge production, so that the nitrogen available for nitrification in raw and settled wastewater are approximately equal. Temperature has little effect on the different concentrations of nitrogen. However,

*This depends on the state of the sewage; if the sewage is "fresh" a larger fraction of the TKN can still be in particulate proteinaceous form.

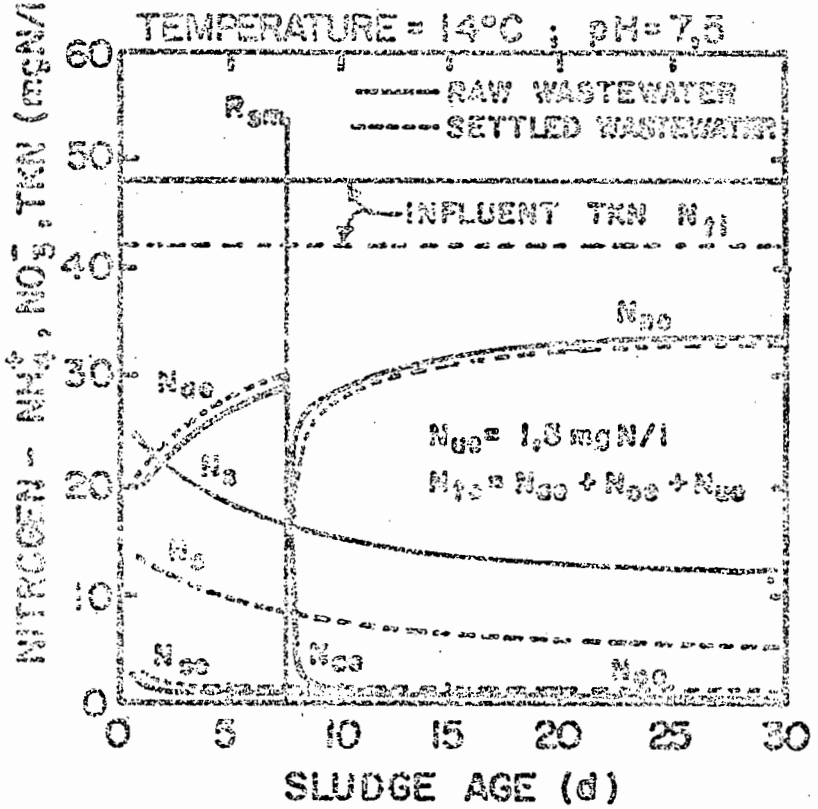

Fig 5.9a

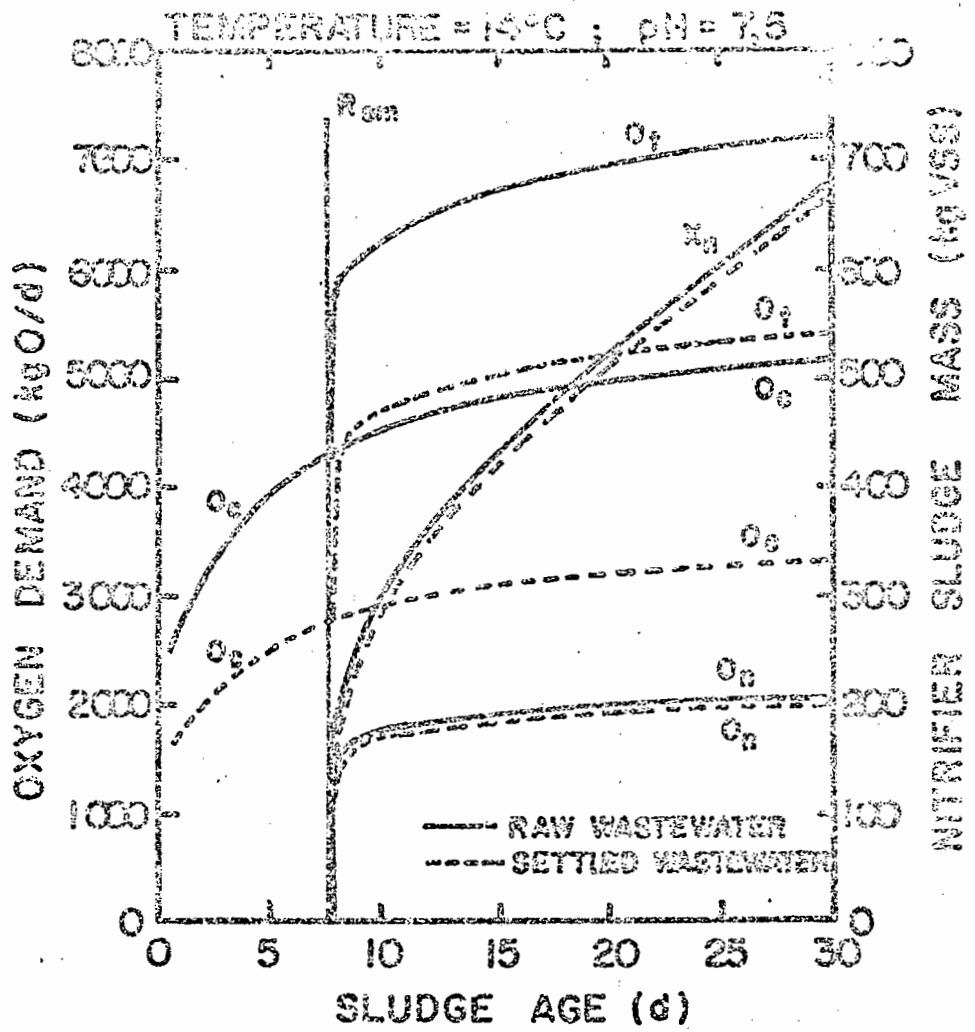

Fig 5.9b

Fig 5.9 *Effluent ammonia (N_{ae}), organic nitrogen (N_{oe}), and nitrate (N_{ne}) concentrations and nitrogen required for sludge production (N_s) (Fig. 5.9a), carbonaceous (O_c), nitrification (O_n), and total (O_t) oxygen demand and the nitrifier sludge mass (X_n) (Fig. 5.9b) versus sludge age for raw and settled wastewater at 14°C*

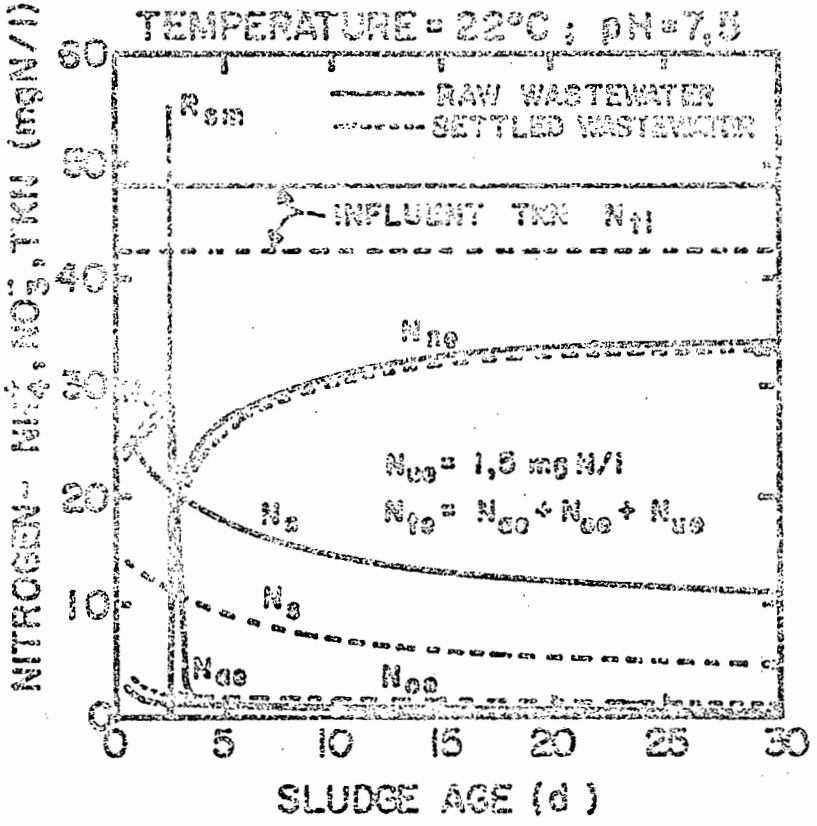

Fig 5.10a

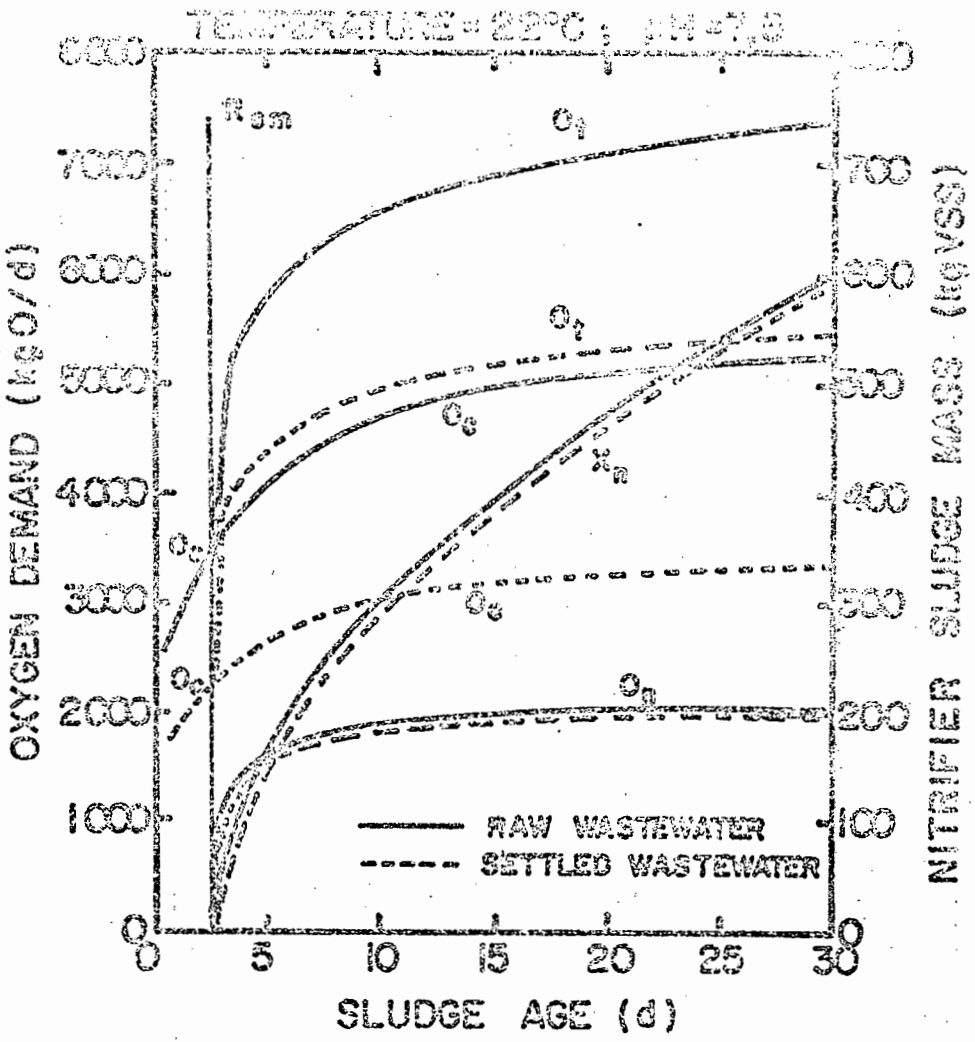

Fig 5.10b

Fig 5.10 *Effluent ammonia (N_{ae}), organic nitrogen (N_{oe}), and nitrate (N_{ne}) concentrations, nitrogen required for sludge production (N_s) (Fig.5.10a) carbonaceous (O_c), nitrification (O_n), and total (O_t) oxygen demand and the nitrifier sludge mass (X_n) (Fig.5.10b) versus sludge age for raw and settled wastewater at 22°C*

a change in temperature causes a significant change in the minimum sludge age for nitrification.

Considering Figs 5.9a and 5.10a, the effluent organic nitrogen concentration (N_{oe}) is less than 2 mgN/ℓ for all sludge ages greater than about 3 days. For sludge ages about 25 percent longer than the minimum for nitrification, the effluent ammonia concentration (N_{ae}) is less than 1 mgN/ℓ so that for $R_s > 1{,}25\ R_{sm}$ the effluent TKN concentration can be taken to be approximately 4 mgN/ℓ. The increase in nitrate concentration (N_{ne}) with increase in sludge age is principally attributable to the reduction in the nitrogen required for sludge production (N_s). This is important for nutrient removal plants as it indicates that increasing the sludge age of a process, increases the nitrification capacity (see section 5.2 above) even though the effluent TKN concentration remains constant at about 4 mgN/ℓ (see Fig 5.8). For $R_s < R_{sm}$, the effluent ammonia concentration (N_{ae}) and hence the effluent TKN concentration (N_{te}), increases with increasing sludge age up to R_{sm} because N_s reduces for increases in R_s.

Figures 5.9b and 5.10b show that the nitrification oxygen demand increases rapidly once $R_s > R_{sm}$ but if $R_s > 1{,}25\ R_{sm}$, the increase is marginal irrespective of the temperature or wastewater type, i.e. between sludge ages 10 and 30 days about 2000 kgO/d are required for nitrification. This nitrification oxygen demand represents an increase of 40% and 60% respectively* above the carbonaceous oxygen demand for the raw and settled wastewater. However, the *total* oxygen demand for treating settled wastewater is only 75% of that treating raw wastewater.

In order that nitrification can proceed without inhibition by oxygen limitation, it is important that the aeration equipment is adequately designed to supply the total oxygen demand; generally heterotrophic organisms growth takes precedence over nitrifier

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*Roughly for $R_s > 1{,}25\ R_{sm}$, the increase in the total oxygen demand due to nitrification is given by $M(O_t) = (1 + 5\ f_{ns})M(O_c)$ where f_{ns} is the TKN/COD ratio of the wastewater. For processes including denitrification see Chapter 6, Section 7.6.2.

growth when oxygen supply becomes insufficient. This is because heterotrophic organisms can grow adequately with dissolved oxygen concentrations of 0,5 to 1,0 mgO/ℓ whereas nitrifiers require a minimum concentration of 1 to 2 mgO/ℓ.

The nitrifiers sludge mass given in Figs 5.9b and 5.10b shows a rapid increase once $R_s > R_{sm}$ and is approximately the same for raw or settled sewage, but is slightly higher at 14°C than at 22°C. Comparing the nitrifier sludge mass to the heterotrophic sludge mass, even at high TKN/COD ratios, the nitrifier sludge mass comprises only about 2 percent of total volatile mass and may be neglected in the determination of the volatile solids concentration in the activated sludge process treating domestic wastewaters.

It is worth repeating that primary sedimentation removes only a minor fraction of the TKN but a significant fraction of COD. Even though the settled wastewater has a lower TKN than the raw wastewater the process effluent nitrate concentration will not reflect this difference beause the nitrogen removed for sludge production is lower for settled than for raw wastewater. Consequently the nitrate generated is approximately the same for both waste flows. In contrast, the maximum denitrification possible (denitrification potential) in the process is dependent principally on the influent COD concentration and this concentration, we have seen, is significantly reduced by primary sedimentation. This may result in a situation that it may be possible to obtain complete nitrate removal when treating raw wastewater but highly unlikely when treating settled wastewater. This difference in removal can have a profound effect on the process design for biological excess phosphorus removal.

7. REFERENCES

1. Arkley M and G v R Marais (1982) Effect of the anoxic sludge mass fraction on the activated sludge process. Research Report No W 38, Dept. of Civil Eng., Univ. of Cape Town.

2. Dold P L, G A Ekama and G v R Marais (1980) A general model for the activated sludge process. Prog. Wat. Tech., 12, 47-77.

3. Downing A L, H A Painter and G Knowles (1964) Nitrification in the Activated Sludge Process, J Proc.Inst.Sew/Purif., 64, 2, 130-158.

4. Ekama G A, A C van Haandel and G v R Marais (1979) The present status of research on nitrogen removal: a model for the modified activated sludge process. Presented at the Symposium on nutrient removal, S A Branch of the IWPC, Pretoria, May 1979. Proc. published by Water Research Commission of South Africa.

5. Herbert D (1958) Recent progress in microbiology. VII. International congress on microbiology. Ed. by Tunevall, Alinquist and Wiksell, Stockholm, 1958, 381-396.

6. Loewenthal R E and G v R Marais (1977) Carbonate Chemistry of Aquatic Systems: Theory and Application, Ann Arbor Science, Michigan, U S A.

7. Loveless J E and H A Painter (1968) The Influence of Metal Ion Concentration and pH Value in the Growth of a *Nitrosomonas* Strain Isolated from Activated Sludge, Jour.Gen.Micro., 52, 1-14.

8. Malan W N and E P Gouws (1966) Geaktiveerde Slyk vir Rioolwatersuiering op Bellville, Research Report, Council for Scientific and Industrial Research, Nov. 1966.

9. Monod J (1950) Technique of Continuous Culture - Theory and Application, (Translation from French), Ann.Inst.Pasteur, 79, 167.

10. Neytzel-de-Wilde F G (1977) Treatment of Effluents from Ammonia Plants - Part 1. Biological Nitrification of an Inorganic Effluent from a Nitrogen-Chemicals Complex, Water S.A., 3, 3, 113-122.

11. Stenstrom M K and R A Poduska The effect of dissolved oxygen concentration on nitrification. Water Research, 14, 6, 643-649.

12. Van Haandel A C and G v R Marais (1981) Nitrification and Denitrification in the Activated Sludge Process, Research Report W 42, Dept. of Civil Eng., Univ. of Cape Town.

CHAPTER SIX

BIOLOGICAL NITROGEN REMOVAL

by

G A Ekama and G v R Marais

1. PROCESS FUNDAMENTALS

In this chapter the kinetics of the single sludge nitrification denitrification process will be considered in detail. It will be shown that for municipal wastewaters, significant or even complete, removal of nitrate is possible with this process.

There are two main biological activities whereby nitrogen is removed from the wastewater: (1) sludge production and (2) respiration for energy abstraction from organic compounds. These two reactions differ fundamentally in their biological objectives.

1.1 Nitrogen Removal by Sludge Production

The nitrogen removal attributable to sludge production was considered in detail in Chapter 4, Section 9, and it was concluded that for most municipal wastewaters only a minor fraction of nitrogen could be removed by sludge production (see Fig 4.5).

1.2 Biological Denitrification

This biological reaction is known as dissimilative reduction of nitrogen or denitrification and involves the reduction of nitrate or nitrite present in the wastewater to gaseous nitrogen which escapes to the atmosphere. Removal of nitrogen via this process is a consequence of biological redox reactions, to obtain energy from the organic material. In these reactions nitrate and nitrite serve the same function as oxygen, i.e. that of a hydrogen ion/electron acceptor (see Chapter 1).

Nitrate readily replaces oxygen as the terminal electron acceptor because the electron pathway is very similar to that of oxygen. The difference is in the electron transfer from the cytochromes where the specific enzyme reductase is replaced by the enzyme nitrate reductase which catalyses the final electron transfer to nitrate instead of oxygen (see Chapter 1). Studies of pure cultures of denitrifying organisms indicate that the presence of dissolved oxygen prevents the formation of the enzyme necessary for the final electron transfer to nitrate (Chang and Morris, 1972). (See Section 2.2 below

From stoichiometry, it can be shown that when nitrate serves as the terminal electron acceptor, the equivalent mass of oxygen, (as O) if oxygen were the terminal electron acceptor, is

$$1\ mgNO_3 \text{ as } N \equiv 2{,}86\ mgO \text{ as } O \qquad (6.1)$$

Knowing the equivalence between nitrate and oxygen, nitrate consumption for synthesis of new organism mass can be formulated with the equations for oxygen consumption by only slight modification. It also allows COD balances to be properly executed on denitrification processes.

1.3 Effect of Denitrification on Oxygen Demand

In Chapter 5, Section 1, it was shown that when 1 mgN ammonia or TKN is converted to nitrate 4,57 mgO are required. In the section above it was shown that when 1 mgN nitrate is denitrified it is equivalent to 2,86 mgO being supplied. Thus for nitrification, 4,57 mgO/mgN are required, but in denitrification 2,86 mgO/mgN can be recovered, i.e. with denitrification 2,86/4,57.100 = 63% of the oxygen demand for nitrification can be recovered, if complete denitrification is achieved. Because the oxygen requirement for nitrification is about 25 to 35% of the total oxygen requirement, a saving of 15 to 20% of the total oxygen requirement can be made by including biological denitrification. This is demonstrated in Fig 6.1 where the oxygen demand for (i) carbonaceous, (ii) total including nitrification and (iii) total including nitrification and denitrification (per kgCOD load) is plotted

versus sludge age for a typical raw wastewater (see Tables 4.3, 5.2 and 6.1).

Other advantages of processes including denitrification are discussed in Chapter 4, Section 11.2; see also Chapter 5, Section 4,3 and Chapter 6, Section 1.4.

1.4 Effect of Denitrification on Alkalinity

Biological denitrification in which nitrate is reduced to nitrogen gas is accompanied by an increase in Alkalinity. From stoichiometry, for 1 mgN nitrate denitrified, 3,57 mg as $CaCO_3$ Alkalinity is produced. In Chapter 5, Section 4.3 it was shown that in the nitrification process, 7,14 mg/ℓ as $CaCO_3$ alkalinity was lost for every 1 mgN/ℓ ammonia nitrified. Consequently, through denitrification, half the decrease in alkalinity due to nitrification can be recovered.

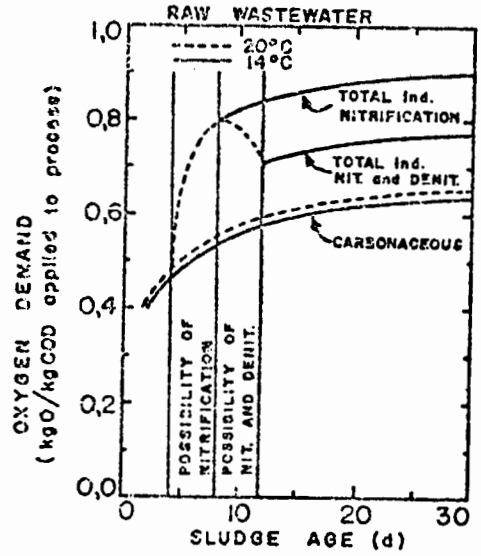

Fig 6.1 *Carbonaceous, total including nitrification and total including nitrification and denitrification oxygen demand per unit COD load versus sludge age for raw wastewater.*

The recovery of alkalinity by denitrification is important when treating wastewaters with low alkalinity values - less than 200 mg/ℓ as $CaCO_3$. For such wastewaters the production of only 15 mgN/ℓ nitrate without denitrification will reduce the mixed liquor pH value to below 5. In this event, because nitrification is extremely sensitive to pH values below 7, only partial nitrification will be obtained, even at long sludge ages. However, should denitrification be incorporated in the process, the recovery of alkalinity by denitrification usually will cause the mixed liquor pH value to be maintained near 7 even for low alkalinity wastewaters. This favourable effect, of maintaining the mixed liquor pH value near 7, makes a nitrification - denitrification process virtually mandatory for activated sludge processes treating wastewaters with low alkalinity values. This aspect is discussed in detail in Chapter 5, Section 4.3 and Chapter 4, Section 11.2.

2. REQUIREMENTS FOR DENITRIFICATION

For denitrification to occur, the following conditions are necessary:

(1) Presence of nitrate (or nitrite)
(2) Absence of dissolved oxygen
(3) A facultative bacterial mass
(4) Presence of a suitable electron donor (energy source).

2.1 Presence of Nitrate

Normally the presence of nitrate implies nitrification as a prerequisite. The conditions for adequate nitrification in an activated sludge process have been discussed in detail in Chapter 5, Section 4. The prerequisite for nitrification involves the estimation of the maximum sludge mass fraction which may be left unaerated but still ensuring nitrification.

2.2 Absence of Dissolved Oxygen

The inhibitory effect of dissolved oxygen on denitrification has been extensively reported in the literature. In a comparative test series, Carlson (1972) found that at zero dissolved oxygen level the nitrate

removed was 100 percent, while at 0,2 mg/ℓ dissolved oxygen (2 to 10 percent oxygen saturation), no significant denitrification was obtained. Furthermore, it should be remembered that in a completely mixed anoxic reactor, even if no measurable dissolved oxygen concentration (D.O.) is present, any oxygen entering such a reactor will be utilized preferentially by the organism mass, thereby reducing (in stoichiometric proportion) the mass of nitrate the reactor can denitrify. Possible sources of D.O. are; (1) high D.O. concentrations in the recycles from the aerobic zones to the anoxic zones - the D.O. concentration should be controlled to be between 1 and 2 mgO/ℓ i.e. sufficiently high so as not to inhibit nitrification in the aerobic reactor but not too high to reduce significantly the denitrification in the anoxic reactor; (2) entrainment into the anoxic reactor via the air-water interface due to unnecessarily high mixing intensitites; (3) Archimedian screw pumps for recycle pumping (4) hydraulic jumps, cascades and shooting flow conditions in interconnecting channels - closed channels and tranquil flow conditions entrain less oxygen. (See also Chapter 10 on operation of nutrient removal plants).

2.3 Facultative Bacterial Mass

The propensity to denitrify is widespread among bacteria. Dissimilative denitrification with end products N_2, NO and NO_2 has been established in numerous cases. The bulk of the bacterial mass in wastewater treatment is facultative and a significant fraction is capable of dissimilative denitrification. Studies on denitrification tend to support the view that there is little difference between the bacterial masses in processes where nitrification only or nitrification-denitrification takes place. There is little merit therefore in attempting to analyse the bacterial composition of the sludge in detail. A sludge generated under aerobic conditions, when subjected to the appropriate environmental conditions, will show a denitrifying capability immediately and will continue to do so, subsequently without apparent change in reactivity.

2.4 Electron Donor (Energy Source)

The oxidation of carbonaceous compounds with nitrate as electron acceptor i.e. denitrification, provides the energy required by the facultative heterotrophs for synthesis of new mass and endogenous respiration. The

electron donor constitutes the source of the energy. The axis about which all biological denitrification investigations revolve is the energy source which serves as the electron donor in the denitrification process. Denitrification has been investigated for a variety of substances as carbonaceous energy sources. These can be categorised as follows:

(a) Energy sources not present in the wastewater, i.e. *an external carbonaceous energy source* which is added at the denitrification stage of the process. Compounds used as an external energy source include methanol, methane, ethanol, acetone and acetic acid.

(b) Energy sources present in the influent wastewater, i.e. *an internal carbonaceous energy source* which enters the system with the wastewater.

(c) Energy sources which are *self-generated* within the system by the release of nutrient by the organisms in the death phase.

The type of energy source utilised has led to different process configurations for denitrification studies. Usually in municipal wastewater treatment only energy sources (b) and (c) above are of interest as these are sources of energy available in the single sludge activated slu process. However in some nutrient removal plants a readily biodegradable COD source may be added to the anaerobic reactor to improve the biological P removal). (See Chapter 4, Section 8 and Chapter 7, Section 3.3). This practice not only improves P removal but also the removal of nitrate by denitrification as it constitutes the addition of an external energy source (group a). Sources of readily biodegradable COD are acid digester supernatant or some form of organic wastewater with a large readily biodegradable COD fraction such as malting industry wastewater, fruit and vegetable canning factory wastewaters, juicing factory wastewaters etc. The addition of these wastes increases the nitrate removal potential by denitrification because the additional readily biodegradable COD allows the initial rapid rate of denitrification to operate for a longer period of time (see Section 4.1.1 below).

3.0 DENITRIFICATION PROCESS CONFIGURATION

Two basic activated sludge process configurations have been developed for single sludge biological denitrification: (1) the Wuhrmann configuration and (2) the Ludzack-Ettinger configuration.

3.1 The Wuhrmann Configuration

The single sludge nitrification-denitrification system in which endogenous energy release provides the energy source for denitrification was first proposed by Wuhrmann (1964). A schematic presentation of the process is shown in Fig 6.2. It consists of two reactors in series, the first aerobic and the second anoxic. The influent is discharged to the first reactor where aerobic growth of both the heterotrophic and nitrifying organisms takes place. Provided the sludge age is sufficiently long and the aerobic fraction of the system is adequately large, nitrification will be complete in the first reactor.

The mixed liquor from the aerobic reactor passes to the anoxic reactor, also called the *post-denitrification reactor* or *secondary anoxic reactor* where it is kept completely mixed by stirring, but with no aeration. The outflow from the anoxic reactor passes through a settling tank and the underflow is recycled back to the aerobic reactor.

Energy release by the sludge mass due to the death of organisms provides the energy source for denitrification in the anoxic reactor. However, the rate of release of energy is low, so that the rate of denitrification is also low. Consequently, in order to obtain a meaningful reduction of the nitrate concentration in the anoxic reactor, the anoxic fraction of the system must be large and this may cause a breakdown of the nitrification process. Thus, although theoretically the system has the potential to remove all the nitrate, from a practical point this usually is not possible as the anoxic volume fraction will need to be so large that the conditions for nitrification cannot be satisfied particularly if the temperatures are low, below 15°C. Furthermore, in the anoxic reactor, organic nitrogen and ammonia are released through organism death, some of which passes out with the effluent thereby reducing the total nitrogen

removal of the system. To minimise the ammonia content of the effluent, a flash or reaeration reactor may be placed between the anoxic reactor and the settling tank. In this reactor the ammonia is then nitrified to nitrate thereby reducing overall efficiency of the nitrate reduction capability of the process.

3.2 The Ludzack-Ettinger Configuration

Ludzack and Ettinger (1962) were the first to propose a single sludge nitrification-denitrification process utilizing the biodegradable material in the influent as an energy source for denitrification. A schematic presentation of this sytems is shown in Fig 6.3. It consists of two reactors in series, *partially* separated from each other. The influent is discharged to the first reactor which is maintained in an anoxic state by stirring without aeration. The second reactor is aerated and nitrification takes place. As there is only partial separation, the mixed liquor in the first reactor is in communication with that in the second reactor. Due to the mixing action in both reactors, an interchange of the nitrified and anoxic liquors is induced, and the nitrate entering the anoxic reactor is reduced to nitrogen gas. Ludzack and Ettinger reported that the process gave variable denitrification results, probably due to the lack of control of the interchange of the contents of the two reactors.

In 1973, Barnard in developing the Bardenpho process proposed an improvement of the Ludzack-Ettinger process, by completely separating the anoxic and aerobic reactors, recycling the underflow from the settler to the anoxic reactor, and providing an additional recycle from the aerobic to the anoxic reactor (Fig 6.4).

These modifications allow a significant improvement in control over the process performance. The high influent energy source discharged to the anoxic reactor also called the *pre-denitrification reactor* or *primary anoxic reactor*, gives rise to a high rate of denitrification and a substantially higher reduction of nitrate than in the Wuhrmann process, even when the pre-denitrification reactor of this process

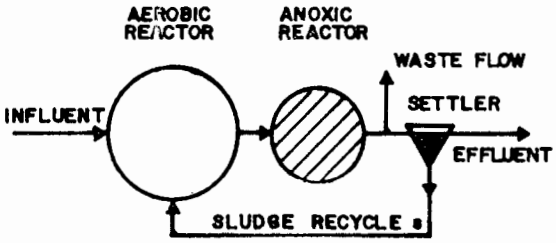

Fig 6.2 *The Wuhrmann process for nitrogen removal.*

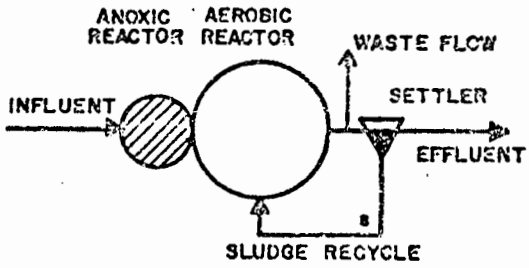

Fig 6.3 *The Ludzack-Ettinger process for nitrogen removal.*

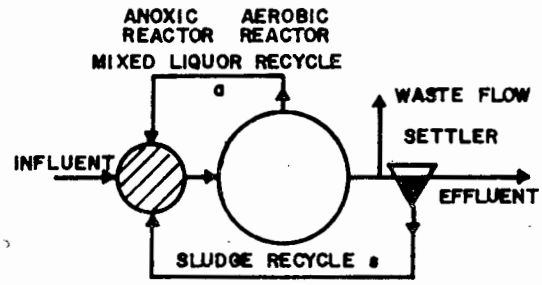

Fig 6.4 *The modified Ludzack-Ettinger process for nitrogen removal.*

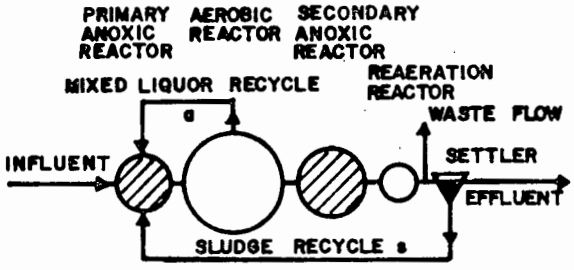

Fig 6.5 *The Bardenpho process for nitrogen removal.*

is substantially smaller than the post-denitrification reactor of the Wuhrmann process. For the purposes of identification, this process will be called the modified Ludzack-Ettinger process.

With the modified Ludzack-Ettinger process, complete denitrification cannot be achieved because a part of the total flow from the aerobic reactor is not recycled to the anoxic reactor but is discharged directly with the effluent.

3.3 The Bardenpho Configuration

In order to overcome the deficiency of incomplete denitrification in the modified Ludzack-Ettinger process, Barnard (1973) proposed combining this process with that of Wuhrmann and called it the Bardenpho process. A schematic presentation of the Bardenpho process is shown in Fig 6.5. Barnard considered that the low concentration of nitrate discharged from the aerobic reactor to the secondary

anoxic reactor will be denitrified to produce a relatively nitrate-free effluent. To strip the nitrogen bubbles generated in the secondary anoxic reactor attached to the sludge flocs, he introduced a flash aeration reactor between the secondary anoxic and the final settling tank. The flash aeration reactor was also considered necessary to nitrify the ammonia released during the sludge residence time in the secondary anoxic reactor. In order to reduce the possibility of flotation of sludge in the settler due to denitrification of residual nitrate, the sludge accumulation in the settler was to be kept to a minimum. This was achieved by having a high recycle rate from the settler, approximately equal to the mean influent flow.

Although in concept the Bardenpho process has the potential for complete removal of nitrate, in practice this is not always possible, an aspect that will be discussed in detail in Section 6 below.

4. EXPERIMENTAL BASIS FOR DENITRIFICATION KINETICS

Carlson (1971) and Christensen and Harremoës (1977) suggested that the kinetic reaction for denitrification by activated sludge mixed liquor can be expressed by

$$dN_n/dt = KX \qquad (6.2)$$

where

dN_n/dt = denitrification rate (mgN nitrate/litre/unit time)

N_n = nitrate concentration (mgN/ℓ)

t = time (hours or days)

X = volatile solids concentration (mgVSS/ℓ)

K = specific denitrification constant (mgN/mgVSS/time).

This expression for the denitrification rate was developed from batch tests. It indicates that the nitrate-time relationship is linear and independent of the nitrate concentration, i.e. the rate is zero order with respect to nitrate concentration, and a function only of the volatile sludge concentration.

In order to evaluate Eq (6.2) as a basis for describing denitrification behaviour in the single sludge activated sludge process, Marais and a number of co-workers (Stern, 1974, Wilson, 1976, Marsden, 1977), undertook an extensive investigation into the kinetic behaviour of the modified Ludzack-Ettinger and Wuhrmann configurations using plug flow mixing regimes for the respective primary and secondary anoxic reactors. By measuring the nitrate concentration along the length of the plug flow anoxic reactors, the denitrification kinetic behaviour was determined by plotting nitrate concentration-time profiles. Experiments were carried out using only raw and settled wastewaters at different temperatues, sludge ages, sludge concentrations, influent COD concentrations and recycle ratios.

The investigation was divided into two parts (1) constant flow and load conditions and (2) cyclic flow and load conditions.

4.1 Constant Flow and Load Conditions

4.1.1 Experimental Work with Plug Flow Reactors

Typical nitrate concentration-time profiles for secondary and primary anoxic plug flow reactors are shown in Figs 6.6 and 6.7 respectively. The secondary anoxic profiles all exhibited a single linear phase that appeared to be independent of the nitrate concentration i.e. the profiles exhibited a behavioural pattern not at variance with Eq (6.2). The primary anoxic profiles, however, exhibited profiles that all indicated a two-stage denitrification response,i.e. (1) a fast primary phase of short duration (1 to 10 minutes), thereafter (2) a slow secondary phase at about one seventh the rate of that of the primary phase.

In order to fit the experimental data into the functional form expressed by Eq (6.2), it is necessary to discuss the following aspects: (i) sludge concentration, (ii) denitrification rate constants, (iii) recycle ratios, and (iv) sludge age.

(i) Sludge Concentration: As the denitrification reaction is mediated by the active organisms, Eq (6.2) should be expressed in terms of the active mass concentration X_a, i.e.

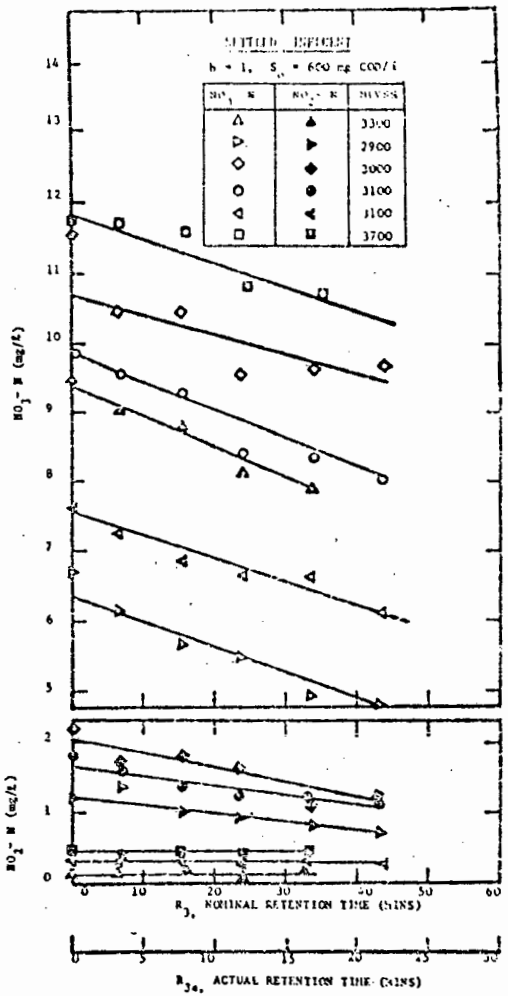

Fig 6.6 *Nitrate concentration profiles observed in a plug-flow secondary anoxic reactor*

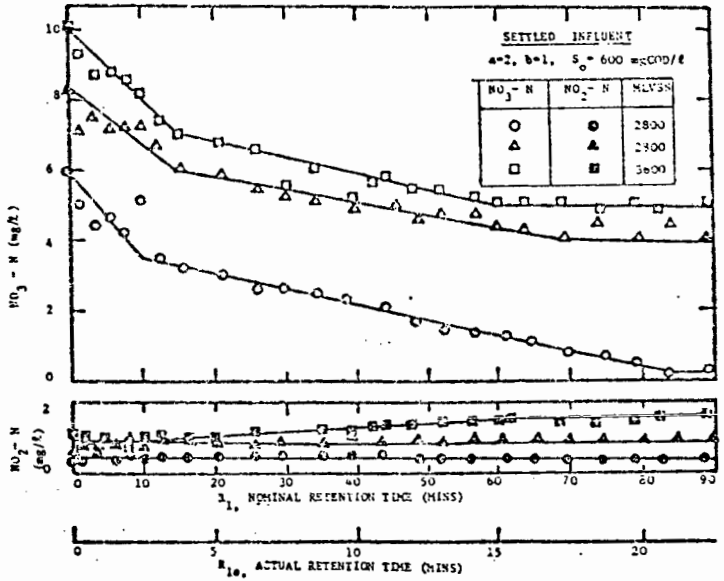

Fig 6.7 *Nitrate concentration profiles observed in a plug-flow primary anoxic reactor at 20°C*

$$N_n = K X_a \Delta t \qquad (6.3)$$

In all the investigations by Marais and his co-workers it was found that the sludge production in anoxic-aerobic systems was not distinguishably different from a comparable aerobic system, provided that the anoxic volume fraction was not goo great (i.e. less than about 50 percent). Consequently, the active mass concentration X_a in the system could be expressed by Eq (4.10) (see Chapter 4, Section 4), (Arkley and Marais, 1982).

(ii) Denitrification Rate Constants, K: If the denitrification rate constant, K, maintains the same value throughout the actual residence time in the plug-flow reactor, R_a, then the difference between the influent and effluent nitrate concentrations, N_{ni} and N_{no} respectively, can be written in terms of Eq (6.2)

$$N_{ni} - N_{no} = \Delta N_{na} = K X_a R_a \qquad (6.4)$$

where

R_a = actual retention time in plug flow reactor (hrs or d)

Equation (6.4) is valid only if the effluent nitrate from the reactor is greater than zero, see Section 4.1.3 below.
The difference $(N_{ni} - N_{no})$ is the *actual* removal of nitrate concentration in the *reactor*. However, as the rate of flow through the reactor is Q (1 + a) (where Q = units of influent flow to the plant per unit of time and a = recycle ratio), the flow passes (a + 1)/1 times through the reactor. This gives the *system* removal, N_{ns}, i.e.

$$\Delta N_{ns} = (a + 1)(N_{ni} - N_{no}) \qquad (6.5)$$

The *nominal* retention time of the plug-flow reactor is defined by

$$R_n = V_r/Q \qquad (6.6)$$

where

R_n = nominal retention time

V_r = volume of the reactor (ℓ)

Q = daily average influent flow to process.

Hence the relationship between the actual and nominal retention times is

$$R_a = R_n/(1 + a) \qquad (6.7)$$

Substituting Eq (6.4) for $N_{ni} - N_{no}$ and Eq (6.7) for R_a into Eq (6.5), the system nitrate removal is given by

$$\Delta N_{ns} = K X_a R_n \qquad (6.8)$$

Comparing Eqs (6.4 and 6.8), note that K is independent of the recycle ratio a. Hence K can be determined directly from Eq (6.4) i.e. from the actual observed reduction in the nitrate concentration in the anoxic reactor. With these basic equations the nitrate reduction in the primary and secondary anoxic reactors now can be formulated.

Secondary anoxic reactor:

Referring to the experimental secondary anoxic reactor profiles, Fig 6.6, only one constant linear nitrate time reduction phase was observed and the analyses above allow the denitrification rate constant in this reactor, K_3 to be determined directly from Eq (6.4) i.e.

$$\Delta N_{nss} = K_3 X_a R_{ns} \qquad (6.9)$$

where the additional subscript s refers to the secondary anoxic reactor.

By applying Eq (6.9) to all the profiles observed experimentally, a set of K values was obtained at 14°C and 20°C respectively and the mean value determined by a graphical statistical analysis.

The statistical plot of the K_3 values obtained at 14°C is shown in Fig 6.8. From the mean K_3 values at 14°C and 20°C the effect of temperature on K_3 was formulated as

$$K_{3T} = 0{,}072\ (1{,}03)^{T-20} \quad (mgNO_3\text{-}N/mgVASS/d) \qquad (6.10)$$

Primary anoxic reactor:

Referring to the primary anoxic reactor profiles, two linear reduction phases were observed. The first phase persisted only for a limited period, the second phase persisted for the remaining retention time in the plug flow reactor, see Fig 6.7. To determine the denitrification rate constants of the two phases, it was presumed that the second phase was also operative during the first phase i.e. the slope of the nitrate-time profile of the first phase is the sum of the slopes of the two phases; the slope of the first phase is governed by $(K_1 + K_2)$. Later it will be shown that there is good reason to believe that this is indeed so - see Section 4.1.2 below. The separation of the phases and their associated K values are best appreciated by graphically setting out the nitrate-time profile as shown in Fig 6.9. Hence the *system* reduction in the pre-denitrification reactor can be written:

$$\begin{aligned} \Delta N_{nps} &= \Delta N_{n1s} + \Delta N_{n2s} \\ &= K_1 X_a t_1 (a + 1) + K_2 X_a R_{ap} (a + 1) \\ &= K_1 X_a t_1 (a + 1) + K_2 X_a R_{np} \end{aligned} \qquad (6.11)$$

where

t_1 = duration of the first denitrification phase; subscripts 1 and 2 refer to the first and second phases of denitrification; subscript p refers to the primary anoxic or pre-denitrification reactor; subscripts a and n on the R parameter refer to actual and nominal retention times respectively.

From the many experimental profiles the values of K_1 and K_2 were calculated using the construction set out in Fig 6.9, and Eq (6.11). The statistical plots of the K_1 and K_2 values at 14°C and 20°C are shown in Fig 6.10. From the mean values at these two temperatures, the following temperature dependency equations were obtained,

$$K_{1T} = 0{,}720\ (1{,}20)^{(T-20)} \qquad (mgNO_3\text{-}N/mgVASS/d) \qquad (6.12)$$

$$K_{2T} = 0{,}1008\ (1{,}08)^{(T-20)} \qquad (mgNO_3\text{-}N/mgVASS/d) \qquad (6.13)$$

for $T \geqq 13°C$

$K_{2T} = K_{3T}$ for $T < 13°C$.

The temperature sensitivity of the denitrification rate constants given above and in Eq (6.10) can be considered reliable only in the range 12°C to 24°C.

From the experimental data as analysed above, Marais and co-worker came to the conclusion that the system reduction of nitrate in the first phase of denitrification, ΔN_{nls}, was approximately proportional to the influent *biodegradable* COD concentration, S_{bi} (see Eq 2.7) i.e.

$$\Delta N_{nls} = \alpha\ S_{bi} \qquad (6.14)$$

Experimentally, for raw or settled wastewater, the mean value of α was found to be 0,028 mgN/mg *biodegradable* COD, and this value of α appeared to be independent of temperature. Taking account of these characteristics, the system nitrate reduction in the primary anoxic reactor can be written as

$$\Delta N_{nps} = \alpha\ S_{bi} + K_2 X_a R_{np} \qquad (6.15)$$

and the duration of the first phase of denitrification can be found from Eq (6.11) as

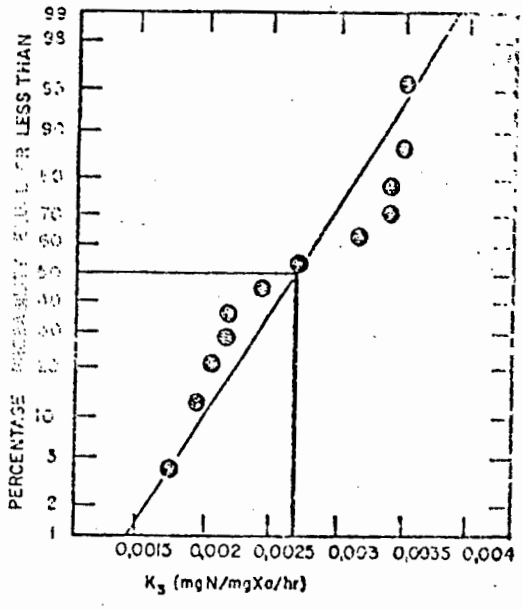

Fig 6.8 *Statistical plot of the observed denitrification rate constants in a secondary anoxic reactor (K_3).*

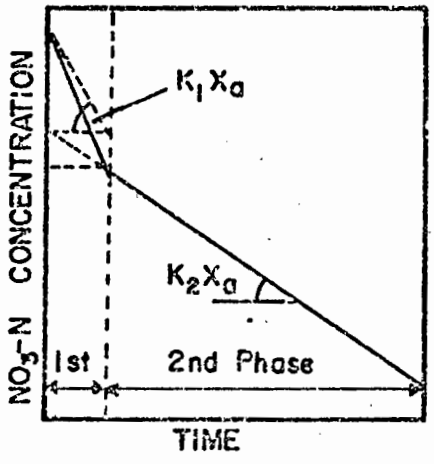

Fig 6.9 *Denitrification rate constants K_1 and K_2 in a primary anoxic reactor.*

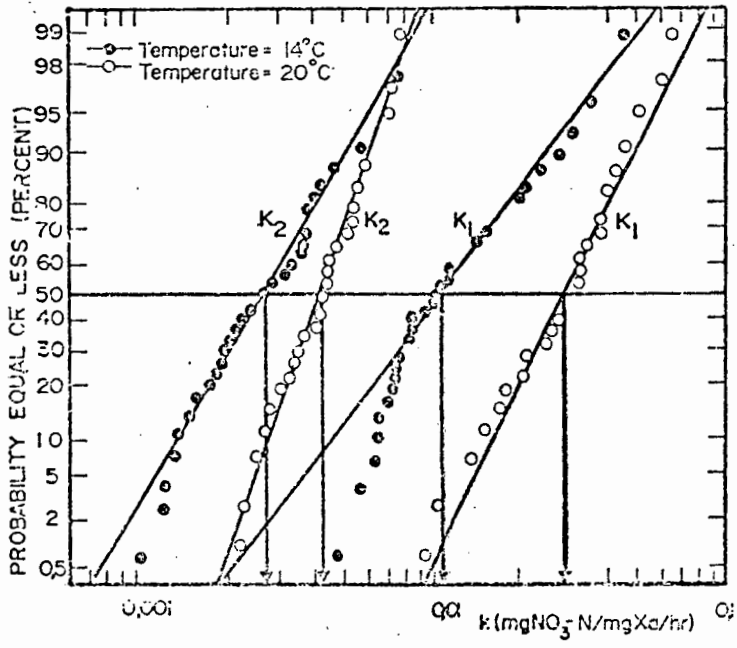

Fig 6.10 *Statistical plots of denitrification rate constants K_1 and K_2 (pre-denitrification) at 14°C and 20°C.*

$$t_1 = \alpha S_{bi}/\{K_1 X_a (1 + a)\} \quad (6.16)$$

From Eq (6.16), the duration of the first phase of denitrification in the primary anoxic reactor, t_1, depends on the recycle ratio and the active mass concentration. Usually t_1 lies in the range 2 to 10 minutes.

(iii) Recycle Ratios:

The total system nitrate reduction of the primary and secondary anoxic reactors is the sum of Eqs (6.9 and 6.15) i.e.

$$\Delta N_{nts} = \alpha S_{bi} + K_2 X_a R_{np} + K_3 X_a R_{ns} \quad (6.17)$$

where

ΔN_{nts} = total system nitrate removal.

An important point to note is that Eq (6.17) is valid only if the nitrate is not reduced to zero in any one of the anoxic reactors. Where this condition is satisfied,then from Eq (6.17) the magnitude of the recycle ratio does not affect the system reduction. However, there must be a minimum recycle; this is determined by the recycle value that *just* causes the nitrate to be zero at the end of a plug flow reactor. If the recycle is less, the nitrate will become zero before the end of the reactor is reached - the recycle can be increased (with concomitant increase in the nitrate removal) to the point where nitrate *just* starts to appear in the effluent. Once nitrate appears in the effluent from all the anoxic reactors, a further increase in the recycle will have no effect on the system nitrate reduction.

(iv) Sludge Age:

Marais and co-workers found experimentally that at a specific temperature the value of the respective denitrificatior

constants appeared to remain unchanged irrespective of the sludge age for sludge ages between 10 and 25 days.

4.1.2 Nitrate removal and substrate utilization

It has been established in the biological growth kinetic theory that for the utilization of 1 mgCOD under aerobic conditions, an amount of $(1-f_{cv}Y_h)$ mg oxygen is required. Numerically with f_{cv} = 1,48 mgCOD/mgVSS and Y_h = 0,45 mgVSS/mgCOD, the oxygen consumption per substrate utilization is 0,33 mgO/mgCOD (Chapter 1, Section 4). In an anoxic reactor with substrate utilisation, nitrate is reduced instead of oxygen. As the oxygen equivalent of nitrate is 2,86 mgO/mgN (from Eq 6.1), the nitrate consumption per mgCOD utilised is $(1-f_{cv}Y_h)/2,86$ = 0,116 mgN/mgCOD or conversely 8,6 mgCOD are required to reduce 1 mgN nitrate. From Eq (6.14) the nitrate concentration removed during the first phase of denitrification is αS_{bi} where α = 0,028 and S_{bi} = biodegradable influent COD concentration. Thus the COD reduction during the first phase of denitrification is $0,028.8,6.S_{bi}$ = 0,24 S_{bi}. From measurements of the readily biodegradable COD in the influent feed, it was found from Eq (2.8) that the readily biodegradable COD fraction f_{bs} of raw wastewater was 0,24. It was therefore hypothesized that the rapid first phase of denitrification is associated with the utilization of the readily biodegradable COD of the influent. It was also hypothesized that the second slower denitrification rate in the primary anoxic reactor and the rate in the secondary anoxic reactor are associated with the utilization of the slowly biodegradable particulate COD. From a simulation study of the denitrification behaviour in primary and secondary plug flow anoxic reactors, it was concluded that both these hypotheses appear to be valid. Details of this work (see van Haandel and Marais, 1981) are not important here, however, the following conclusions are: (i) the utilization of readily biodegradable COD and slowly biodegradable COD take place simultaneously (see Section 4.1.1 and Fig 6.9 above), and (ii) the second rate in the primary anoxic reactor (K_2) and the rate in the secondary anoxic reactor (K_3) both arise from the utilization of particulate slowly biodegradable COD but the K_2 is more

rapid than K_3 because the concentration of slowly biodegradable COD in the primary anoxic reactor is higher than that in the secondary anoxic reactor - in the primary anoxic reactor the slowly biodegradable COD arises from that in the influent and organism death whereas that in the secondary anoxic reactor arises from organism death only.

4.1.3 Completely mixed anoxic reactors

Up to this stage, only plug flow reactors have been considered. Although this flow regime is important from a research point of view, it has little practical application in full scale nitrification-denitrification plants. Because the denitrification reaction in an anoxic reactor is approximately zero order with respect to nitrate, the reduction achieved in a reactor is virtually independent of the flow regime. Consequently, the equation developed for the nitrate reduction, Eq (6.17) should be valid also for completely mixed reactors. Where the plug flow reactors were replaced by completely mixed reactors of the same volume, experimental data indicate that the reductions are substantially the same.

Generally, completely mixed reactors are not useful to obtain basic time behaviour characteristics as it is possible only to measure influent and effluent concentrations. However, if the reduction is a single zero order reaction (as in the case of the secondary anoxic reactor), the correct K value can be calculated from the influent and effluent nitrate concentrations (provided the latter is not zero) but if the reduction is due to two zero order reactions (as in the case of the primary anoxic reactor), the correct K values cannot be separated out; the combined effect of the two K values is to give rise to an apparent K value that varies with the retention time. This point is mentioned because in many instances the literature gives primary anoxic denitrification rate constants calculated from influent and effluent nitrate concentrations from completely mixed primary anoxic reactors. A further cause of error is that the denitrification rate constants in the literature often are given in terms of mg nitrate removed per

mg *volatile suspended solids* per unit time. Constants reported in terms of total VSS should be used with caution because the denitrification rates are first order with respect to the *active* volatile suspended solids (X_a) (see Eq 6.3), not first order with respect to the total volatile suspended solids (X_v) - the inert fraction of the VSS varies significantly with sludge age and wastewater type (see Fig 4.2), so that the denitrification rate constants in terms of total VSS cannot be applied to wastewaters and sludge ages different to those on which the rates were measured. However, if the wastewater characteristics, sludge age and temperature are known then, via the activated sludge theory given in Chapter 4, the denitrification rate constant, if given in terms of VSS, may be corrected to be in terms of the active volatile solids concentration.

4.2 Cyclic Flow and Load Conditions

When denitrification experiments were run under cyclic loading conditions, the approach outlined above for calculating the extent of denitrification no longer appeared to be applicable - the total nitrate concentration removed was less than observed under steady state loading conditions, the removal of nitrate decreased as the severity of the cyclic load variation increased, and the TKN in the effluent showed a marked cyclic response, being high during the high loading phase and low during the low loading phase, whereas the nitrate behaved in exactly the opposite fashion. It was evident that to establish a general denitrification model, an alternative approach to that established for analysing the steady state behaviour was needed. This was sought in the general model for the activated sludge process developed by Ekama and Marais (1978). The details of this research work are not essential for using this monograph, but it can be mentioned that a large measure of success was achieved in predicting the behaviour of denitrification under dynamic loading conditions once a number of modifications to the model of Ekama and Marais (1978) were accepted. Interested readers are referred to the following publications: Dold, Ekama and Marais (1980); Ekama, van Haandel and Marais (1979); Siebritz, Ekama and

Marais (1980); van Haandel and Marais (1981); van Haandel, Ekama and Marais (1981) and van Haandel, Dold and Marais (1982).

The outcome of the research work described in the references above, was a general dynamic model of the activated sludge process including nitrification and denitrification. The theoretical predictions of the general model correlated well with the experimental data observed under both constant and cyclic loading conditions at laboratory and pilot scale.

The general dynamic model, which describes the activated sludge process in basic biological mechanisms, was utilised to study the validity of the empirical denitrification constants K. A comparison of the theoretically predicted and experimentally observed K values is given in Figs 6.11 and 6.12. These figures show that for sludge ages between 10 and 30 days and temperatures between 12 and 22°C, good correlation between simulated and experimental K values is obtained. The good correlation indicates that although the K values are empirical and

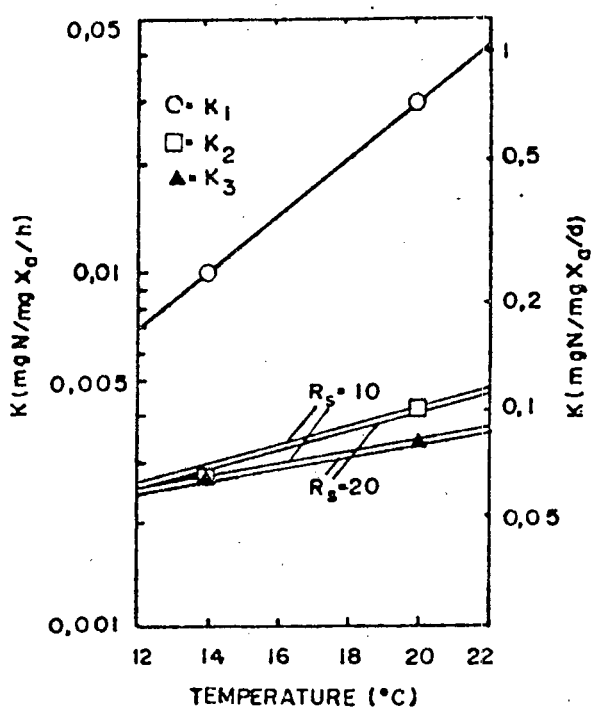

Fig 6.11 *Simulated and experimental denitrification rate constants K_1, K_2 and K_3 versus temperature for 10 and 20 days sludge age.*

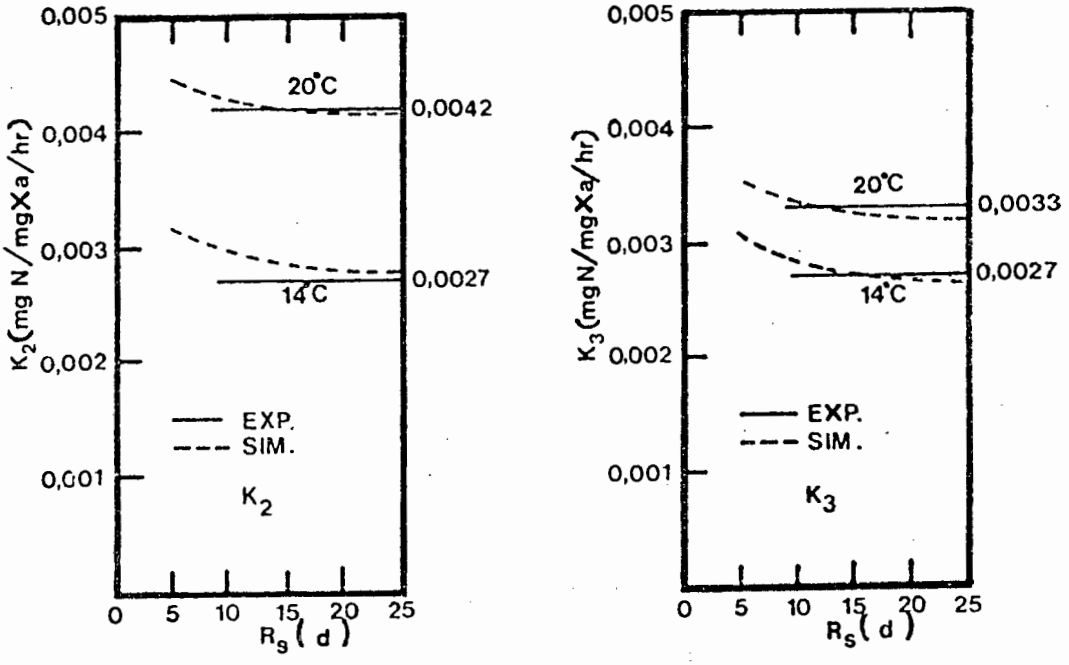

Fig 6.12 *Simulated and experimental denitrification rate constants K_2 and K_3 versus sludge age at 14°C and 20°C.*

have no fundamental biological kinetic basis (of the kind on which the general dynamic model is based), they nevertheless appear to have such consistency that they can be applied to the design of anoxic reactors for constant loading conditions.

5.0 DENITRIFICATION POTENTIAL

From the empirical denitrification equation of the primary and secondary anoxic reactors, Eqs (6.15 and 6.9), it is clear that there is a maximum concentration of nitrate that can be removed by the anoxic reactors. In terms of these equations, this maximum for the primary anoxic reactor depends on the influent biodegradable COD, the active mass concentration and the retention time, and for the secondary anoxic reactor only on the active mass concentration and the retention time. The maximum concentration of nitrate that can be removed by an anoxic reactor is known as the *denitrification potential* of the reactor.

5.1 Denitrification Potential of the Primary Anoxic Reactor

From Eq (6.15), the denitrification potential of the primary anoxic reactor, D_{p1} is given by

$$D_{p1} = \alpha S_{bi} + K_2 X_a R_{np} \qquad (6.18)$$

Now $X_a R_{np} = X_a V_a / Q$ (where V_a = volume of the primary anoxic reactor and Q = daily average influent flow). The term $X_a V_a$ represents the mass of sludge in the primary anoxic reactor, which can be expressed as a fraction of the total mass of sludge in the process. Let f_{x1} be the mass of sludge in the primary anoxic reactor as a fraction or the total mass of sludge in the process i.e. the primary anoxic sludge mass fraction, then from Eq (4.10)

$$\begin{aligned} X_a V_a &= f_{x1} M(X_a) \\ &= f_{x1} Y_h R_s Q S_{bi} / (1 + b_h R_s) \end{aligned}$$

Dividing through by Q

$$X_a V_a/Q = f_{x1}\ Y_h R_s S_{bi}/(1 + b_h R_s) \qquad (6.19)$$

Substituting the RHS of Eq (6.19) for $X_a R_{np}$ into Eq (6.18) yields

$$D_{p1} = S_{bi}\ \{\alpha + K_2 f_{x1} Y_h R_s/(1 + b_h R_s)\} \qquad (6.20)$$

where

D_{p1} = denitrification potential of the primary anoxic reactor (mgN/ℓ influent)

S_{bi} = biodegradable COD concentration of the influent

α = fraction of nitrate removed by the initial rapid phase of denitrification

= $f_{bs}\ (1 - f_{cv} Y_h)/2,86$ (see Section 4.1.2 above)

where

f_{bs} = readily biodegradable fraction of the influent biodegradable COD

f_{x1} = primary anoxic sludge mass fraction.

In Eq (6.20), it is assumed that the initial rapid rate of denitrification is always complete, i.e. the actual retention time in the primary anoxic reactor is always longer than the time required to utilise all the readily biodegradable COD in the influent, given by t_1 in Eq (6.16). If t_1 is taken to be the minimum actual hydraulic retention time, it can be shown by substituting Eq (4.10) for X_a and Eq (6.16) for t_1, that the minimum primary anoxic sludge mass fraction f_{x1min} to deplete the readily biodegradable COD is

$$f_{x1min} = \frac{f_{bs}(1 - f_{cv} Y_h)(1 + b_h R_s)}{2,86\ K_1 Y_h R_s} \qquad (6.21)$$

Substituting the values of the kinetic constants into Eq (6.21) $f_{xpmin} < 0,08$ for $R_s > 15$ days at 14°C. This value is much lower than most practical primary anoxic reactors so that Eq (6.20) will be valid in most cases.

A diagrammatic representation of Eq (6.20) is given in Fig 6.13 for different primary anoxic sludge mass fractions (f_{x1}) and temperatures. The diagram shows that the denitrification potential of a primary anoxic reactor increases as sludge age, anoxic sludge mass fraction and temperature increase, but that the denitrification potential is most sensitive to the anoxic sludge mass fraction (f_{x1}).

5.2 Denitrification Potential of the Secondary Anoxic Reactor

The denitrification potential of the secondary anoxic reactor is found in a similar fashion as that for the primary anoxic reactor and is found to be given by

$$D_{p3} = S_{bi}\, f_{x3}\, K_3\, Y_h\, R_s \,/\, (1 + b_{hT} R_s) \qquad (6.22)$$

where

D_{p3} = denitrificaction potential of the secondary anoxic reactor (mgN/ℓ influent)

f_{x3} = anoxic sludge mass fraction of the secondary anoxic reactor.

A diagrammatic representation of Eq (6.22) is given in Fig 6.13 for different anoxic sludge mass fractions and temperatures. The denitrification potential increases at the sludge ages, temperature and anoxic sludge mass fraction (f_{x3}) increase, but is most sensitive to the anoxic sludge mass fraction (f_{x3}).

6. DESIGN PROCEDURE FOR N REMOVAL PROCESSES

In the preceding sections, four important parameters were defined and discussed. These are (1) maximum unaerated sludge mass fraction (f_{xm}, Chapter 5, Section 4.4), (2) nitrification capacity (N_c, Chapter 5, Section 5.2), (3) denitrification potential (Section 5 above) and the TKN/COD ratio (Chapter 3, Section 4). These parameters greatly facilitate the design of nitrogen removal process. The salient aspects of these four parameters are briefly set out below.

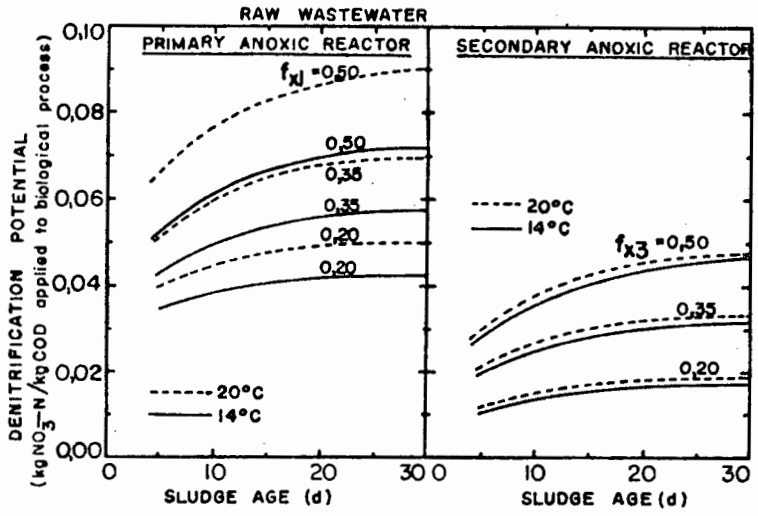

Fig 6.13 *Denitrification potential per kgCOD applied to biological process versus sludge age for primary (left) and secondary (right) anoxic reactors of different unaerated sludge mass fractions (f_{x1} and f_{x3}) for raw wastewater at 14°C and 20°C*

Maximum Unaerated Sludge Mass Fraction

As nitrification is a prerequisite for denitrification the fraction of the sludge mass under aerobic conditions must be sufficiently large to allow complete nitrification. At a particular sludge age, this sets a limit on the fraction of sludge that is not aerated i.e. sets a maximum unaerated sludge mass fraction (f_{xm}). The maximum unaerated sludge mass fraction is dependent principally on the maximum specific growth rate of the nitrifiers at 20°C (μ_{nm20}) attainable with the wastewater, the minimum average temperature of the wastewater, (T_{min}) and the sludge age of the process (R_s). In order to ensure nitrification, it is recommended that f_{xm} is limited at 0,50 to 0,60 and that the minimum aerobic sludge mass fraction is increased by a factor of safety of 1,25 to 1,35 (see Chapter 5, Section 4.4).

Nitrification Capacity of Process

The nitrification capacity is the concentration of nitrate per unit of influent flow that the process produces by nitrification of the influent TKN concentration. If the unaerated sludge mass fraction satisfies the conditions set out above, complete nitrification is likely to take place and the effluent TKN concentration will be between 2 and 3 mgN/ℓ. Under these conditions the nitrification capacity is independent of the process configuration and is the difference between the influent TKN concentration and the sum of the nitrogen required for sludge production and effluent TKN concentration (Chapter 5, Section 5.2).

Denitrification Potential of Process

The denitrification potential of a process is the maximum mass of nitrate per unit influent flow that the process as designed can denitrify. It is directly proportional to the influent biodegradable COD concentration and the position and sizes of the anoxic reactors because denitrification in the primary anoxic reactor is faster than in the secondary anoxic reactor.

The Influent TKN/COD Ratio

Because the nitrification capacity and denitrification potential are approximately proportional to the influent TKN and COD concentrations respectively, the influent TKN/COD ratio is a relative measure of the mass of nitrate generated in the process by nitrification and the mass of nitrate that can be removed in the process by denitrification.

6.1 Principles of the Design Procedure

From the wastewater characteristics i.e. influent TKN and COD concentrations (N_{ti} and S_{ti}), maximum specific growth rate of the nitrifiers

at 20°C (μ_{nm20}), the readily biodegradable COD fraction (f_{bs}) and the minimum average wastewater temperature (T_{min}), the maximum unaerated sludge mass fraction (f_{xm}) and the nitrification capacity (N_c) can be calculated for a selected sludge age (R_s). The f_{xm} then can be subdivided into primary and secondary anoxic sludge mass fractions (f_{x1} and f_{x3}) and this division fixes the denitrification potential of these two reactors and hence also of the process. When considering the subdivision of f_{xm}, it should be remembered that the denitrification potential of the primary anoxic reactor (D_{p1}) is greater than that of the secondary anoxic reactor (D_{p3}) for equal anoxic sludge mass fractions, but that sufficient nitrate must be recycled to the primary anoxic reactor to fully utilize its denitrification potential.

The relative sizes of the primary and secondary anoxic sludge mass fractions (f_{x1} and f_{x3}), as well as whether or not a secondary anoxic reactor is to be included in the process configuration, depend on the influent TKN/COD ratio. If the objective is to remove as much nitrogen as possible, the denitrification potential of the process (which may or may not include a secondary anoxic reactor) must be as close as possible to the nitrification capacity. Complete denitrification is possible only when the process configuration incorporates a secondary anoxic reactor and if the sum of the denitrification potentials of the primary and secondary anoxic reactors is greater than the nitrification capacity, i.e. $D_{p1} + D_{p3} > N_c$ (provided D_{p1} is fully utilized by having a sufficiently high mixed liquor a-recycle).

If complete denitrification is not possible due to a high TKN/COD ratio, nitrate will be present in the effluent. If the effluent nitrate concentration is greater than about 5 to 6 mgN/ℓ, the incorporation of a secondary anoxic reactor becomes an inefficient utilization of the unaerated sludge mass fraction; an improved nitrate removal will be obtained if the secondary anoxic reactor (f_{x3}) is incorporated into the primary anoxic reactor (f_{x1}). Removal of the secondary anoxic reactor from the Bardenpho process (Fig 6.5) reduces the configuration to a Modified Ludzack-Ettinger (MLE) process (Fig 6.4).

The above discussion indicates that in order to select a nitrogen

removal process configuration, it is necessary to check whether or not complete denitrification can be achieved.

6.2 Can Complete Denitrification be Achieved?

In the nitrogen removal processes, the maximum anoxic sludge mass fraction available for denitrification, f_{xdm}, is equal to the maximum unaerated sludge mass fraction f_{xm}, i.e.

$$f_{xdm} = f_{xm} \tag{6.23}$$

where f_{xm} is given by Eq (5.24) for selected R_s, μ_{nmT} and T_{min}.

To check whether or not complete denitrification can be obtained with the maximum anoxic sludge mass fraction, the following reasoning is applied: In the Bardenpho process (which has the potential for complete denitrification), for a fixed underflow s-recycle ratio*, the mixed liquor a-recycle ratio governs the distribution of the nitrate from the aerobic reactor between the primary and secondary anoxic reactors - the higher the a-recycle ratio with respect to the s-recycle ratio, the greater the proportion of nitrate recycled to the primary anoxic reactor. For the selected a- and s-recycle ratio, the best denitrification performance is obtained when the primary anoxic reactor is just loaded to its denitrification potential. If the primary anoxic reactor is loaded to its denitrification potential, the nitrate concentration in the outflow of the reactor is zero and the nitrate concentration in the aerobic reactor is given by $N_c/(a+s+1)$ i.e. the nitrification capacity diluted into the total flow entering the aerobic reactor. Knowing the nitrate concentration in the aerobic reactor and including the effect of the dissolved oxygen concentration (D.O.) in the aerobic reactor and underflow s-recycle, the equivalent nitrate load imposed on the primary and secondary anoxic reactors by the selected a- and s-recycles can be calculated. Now a useful analytical device is to increase the equivalent nitrate load on the secondary anoxic reactor by a factor K_{2T}/K_{3T} so that the reactor acts like a primary anoxic reactor except that it receives no readily

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* Recycle ratios specified with respect to the daily average influent flow rate.

biodegradable COD. Adding the equivalent nitrate load on the primary anoxic reactor to the adjusted equivalent nitrate load on the secondary anoxic reactor, a total equivalent nitrate load is obtained. Because the secondary anoxic reactor has been transformed to act like a primary anoxic reactor, their respective contributions to total denitrification potential of the process need not be known, and the maximum anoxic sludge mass fraction (f_{xdm}) can be assumed to be in the form of a primary anoxic reactor. Consequently the process denitrification potential D_{pp} can be calculated by means of Eq (6.20) with $f_{x1} = f_{xdm}$. Now if the process denitrification potential D_{pp} of the maximum anoxic sludge mass fraction f_{xdm}, is greater or equal to the total equivalent nitrate load, complete denitrification is possible for the selected a- and s-recycle ratios. In contrast, if the D_{pp} of f_{xdm} is less than the total equivalent nitrate load, complete denitrification is not possible for the selected a- and s-recycle ratios, and nitrate will be present in the effluent.

Following the above reasoning and assuming the D.O. concentrations in the a- and s-recycles are O_a and O_s mgO/ℓ respectively, the following equation for the effluent nitrate concentration N_{ne} for the Bardenpho process can be developed:

$$N_{ne} = \frac{\{\frac{N_c}{a+s+1} + \frac{O_a}{2,86}\}\{a + \frac{K_{2T}}{K_{3T}}(s+1)\} + \frac{s.O_s}{2,86} - D_{pp}}{\{\frac{K_{2T}}{K_{3T}} + s(\frac{K_{2T}}{K_{3T}} - 1)\}} \qquad (6.24)$$

where

N_{ne} = effluent nitrate concentration (mgN/ℓ)

N_c = nitrification capacity (mgN/ℓ)

a,s = mixed liquor and sludge underflow recycle ratios respectively

K_{2T},K_{3T} = second denitrification rate in primary anoxic reactor and denitrification rate in secondary anoxic reactor respectively (mgN/mgVASS/d)

O_a,O_s = dissolved oxygen concentration in mixed liquor a and underflow s recycle respectively (mgO/ℓ)

D_{pp} = denitrification potential at temperature T°C on the assumption that the maximum anoxic sludge mass fraction f_{xdm} found from Eq (6.23) is all in the form of a primary anoxic reactor i.e. D_{pp} is given by Eq (6.20) with $f_{x1} = f_{xdm}$ and K_2 adjusted to T°C with Eq (6.13). (6.25)

Also, the optimum primary and secondary anoxic sludge mass fractions f_{x1} and f_{x3}, and the total f_{xdt} are given by

$$f_{x1} = \frac{\{\frac{N_c}{a + s + 1} + \frac{O_a}{2,86})a + (N_{ne} + \frac{O_s}{2,86})s - \frac{f_{bs}(1 - f_{cv}Y_h)\ S_{bi}}{2,86}\}}{\{S_{bi}\ \frac{Y_h R_s}{(1 + b_{hT}R_s)}\ K_{2T}\}} \quad (6.26)$$

$$f_{x3} = \frac{\{(s + 1)\left[\frac{N_c}{a + s + 1} + \frac{O_a}{2,86} - N_{ne}\right]\frac{K_{2T}}{K_{3T}}\}}{\{S_{bi}\ \frac{Y_h R_s}{(1 + b_{hT}R_s)}\ K_{2T}\}} \quad (6.27)$$

$$f_{xdt} = f_{x1} + f_{x3} \quad (6.28)$$

where

f_{x1}, f_{x3}, f_{xdt} = primary, secondary and total anoxic sludge mass fractions respectively.

For a selected sludge age (R_s) and wastewater characteristics (S_{ti}, N_{ti}, f_{bs}, μ_{nm20}, T_{min}, f_{up}, f_{us}) - from which f_{xm} (Eq 5.24), f_{xdm} (Eq 6.23), K_{2T}/K_{3T} (Eqs 6.13 and 6.10), N_c (Eq 5.29) and D_{pp} (Eq 6.25) can be calculated - and selected D.O. concentrations in the a- and s-recycle ratios (O_a and O_s), the only unknowns in Eqs (6.24 to 6.28) are the a- and s-recycle ratios. The s-recycle ratio usually is specified (at say 1) to obtain satisfactory settling tank performance. Hence N_{ne}, f_{x1} and f_{x3} all depend on the a-recycle ratio only, and hence these

three parameters can be calculated for various choices of the a-recycle ratio. If $N_{ne} \leq 0{,}0$ mgN/ℓ for some specified s- and selected a-recycle ratios, then complete denitrification is possible at these recycle ratios.

In the solution procesure, if Eq (6.24) yields $N_{ne} < 0$, N_{ne} must be set equal to zero before substitution into Eqs (6.26 and 6.27). When N_{ne} has to be set equal to zero, it will be noticed that f_{xdt} obtained from Eq (6.28) is less than the f_{xdm} assumed to calculate D_{pp}. The reason for this is that when $N_{ne} < 0$, $D_{pp} > N_c$. By inserting $N_{ne} = 0$ in Eqs (6.26 and 6.27), these equations give f_{x1} and f_{x3} that will *just* produce complete denitrification for the selected a- and specified s-recycle ratios, so that f_{xdt} turns out to be less than f_{xdm}.

For the specified s-recycle ratio, Eqs (6.24 to 6.28) are valid only for a-recycle ratios falling between a lower and an upper limit:

(i) Lower limit; the a-recycle must not be lower than that which gives f_{x1} as calculated from Eq (6.26) less than f_{x1min} as calculated from Eq (6.21) - if $f_{x1} < f_{x1min}$, the readily biodegradable COD is not completely utilized in the primary anoxic reactor leading to inefficient denitrification and also making Eq (6.20) for D_{p1} invalid.

(ii) Upper limit: the a-recycle ratio must not be increased above that which gives f_{x3} from Eq (6.27) a smaller value than that required to remove only the D.O. discharged to the secondary anoxic reactor, i.e. $D_{p3} \geq (1+s)\ O_a/2{,}86$ where D_{p3} is given by Eq (6.22). Hence the minimum secondary anoxic sludge mass fraction is given by

$$f_{x3min} = \frac{(1 + s)\ O_a\ (1 + b_{hT} R_s)}{2{,}86\ S_{bi}\ Y_h R_s\ K_{3T}} \qquad (6.29)$$

Only the a-recycle ratios falling between the lower and upper limits specified above are valid a-recycle ratios.

By analysing the process with a specified s-recycle ratio for increasing values of valid a-recycle ratios, then, if $N_{ne} > 0$, N_{ne} and the optimal subdivision of f_{xdm} into f_{x1} and f_{x3}, or, if $N_{ne} \leq 0$, the total anoxic sludge mass fraction to just obtain $N_{ne} = 0$, f_{xdt}, and its optimal subdivision into f_{x1} and f_{x3} can be plotted versus the a-recycle ratio.

For design purposes where the process is to operate between temperatures T_{min} and T_{max}, the following sequence of calculations needs to be made to check whether complete denitrification can be achieved and if so, to select the optimal process configuration:

Step 1 : Select wastewater characteristics; S_{ti}, N_{ti}, f_{bs}, f_{up}, f_{us}, μ_{nm20}, T_{max}, T_{min}.

Step 2 : Select R_s and S_f.

Step 3 : Calculate f_{xm} for T_{min} from Eq (5.24).

Step 4 : With f_{xm} and R_s calculate S_f for T_{max} from Eq (5.24).

Step 5 : Estimate N_{te} for T_{max} and T_{min}.

Step 6 : With f_{up} and f_{us}, calculate N_s for T_{max} and T_{min} for selected R_s from Eq (4.23).

Step 7 : Calculate N_c from Eq (5.29).

Step 8 : Calculate D_{pp} from Eq (6.20) for T_{max} and for T_{min} with f_{xdm} given by Eq (6.23).

Step 9 : Select s, O_a and O_s.

Step 10 : Calculate f_{x1min} from Eq (6.21) for T_{max} and for T_{min}.

Step 11 : Calculate f_{x3min} from Eq (6.29) for T_{max} and for T_{min}.

Step 12 : Select the a-recycle ratio and calculate N_{ne} for T_{min} from Eq (6.24).

Step 13 : If $N_{ne} < 0$, set $N_{ne} = 0$.

Step 14 : With N_{ne} calculate f_{x1}, f_{x3} and f_{xdt} from Eqs (6.26 to 6.28).

Step 15 : Check that $f_{x1} \geqq f_{x1min}$ and $f_{x3} \geqq f_{x3min}$. If not, discard selected a-recycle ratio as invalid.

Step 16 : Repeat steps 12 to 15 for different a-recycle ratios,

Step 17 : Repeat steps 12 to 16 for T_{max}.

The analysis as to whether or not complete denitrification can be achieved must be undertaken at the *lowest expected temperature* (T_{min}), because the denitrification potential D_{pp} decreases with decrease in temperature. If complete denitrification can be obtained at T_{min} (i.e. $N_{ne} < 0$ from Eq (6.24) for some valid a-recycle ratio at the specified s-recycle ratio), then f_{x1} is fixed at the *highest expected* temperature (T_{max}). In repeating the calculation at T_{max} it will be found that f_{xdt} at T_{max} is less than f_{xdt} at T_{min}, and for a certain a-recycle ratio, there will be a minimum f_{xdt}*. The f_{x1} value corresponding to the minimum f_{xdt} at T_{max} fixes the primary anoxic sludge mass fraction for both T_{max} and T_{min}. Now f_{x3} is fixed at the *minimum expected* temperature (T_{min}) at the f_{x3} value corresponding to the fixed f_{x1} value and the total anoxic sludge mass fraction f_{xdt} for both T_{max} and T_{min} is given by $f_{x1} + f_{x3}$. The f_{x3} is fixed at T_{min} because if it were fixed at T_{max}, then f_{xdt} will be insufficient to achieve complete denitrification at T_{min} because for fixed f_{x1}, f_{xdt} at T_{max} is less than f_{xdt} at T_{min}. With f_{x1} and f_{x3} fixed for

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* If T_{max} is less than about 18°C, a clear minimum cannot be discerned (see Fig 13a for 14°C). In this event any reasonable f_{x1} can be selected with the proviso that complete utilization of the readily biodegradable COD can be *assured* even with a significant decrease in K_{120} (see Eqs 6.12 and 6.21). The existence of a minimum, and the temperatures above which it becomes discernable, depends much on the choice of the D.O. concentration in the recycles O_a and O_s.

both T_{max} and T_{min}, the optimum performance of the process is achieved when it is operated at the a-recycle ratio corresponding to the fixed f_{x1} value, this a-recycle ratio being the optimum a_o. It should be noted that with f_{x1} and f_{x3} fixed,

(i) a_o decreases with decrease in temperature because D_{pl} decreases with decrease in temperature, and

(ii) the use of any a-recycle ratio other than a_o results in a poorer denitrification performance; if $a < a_o$, D_{pl} is not fully utilized and if $a > a_o$, unnecessarily large quantities of D.O. are discharged to the primary anoxic reactor.

In the design of a Bardenpho process for a selected sludge age, if it is found that the total anoxic sludge mass fraction for complete denitrification f_{xdt} is less than the maximum allowed f_{xdm}, the following options are open:

(1) f_{x1} and f_{x3} can be increased to give an f_{xdt} equal to f_{xdm}. This introduces a factor of safety in denitrification by making an allowance for a reduction in the denitrification rates K at 20°C, a reduction in the influent readily biodegradable COD fraction f_{bs} or minimum temperature (T_{min}) or an increase in influent TKN/COD ratio.

(2) The sludge age (R_s) can be reduced so that f_{xdm} becomes equal to f_{xdt}. The lower R_s will allow a saving in process volume (see Fig 4.3). The lower R_s can be estimated as follows: Set f_{xdm} equal to the f_{xdt} required for complete denitrification at T_{min}; determine f_{xm} from Eq (6.23); with f_{xm} calculate R_s from Eq (5.24); to check, repeat step by step procedure with the new R_s.

Option (2) is not as good an alternative as option (1) because it excludes a factor of safety on the nitrogen removal. However, exclusion of a factor of safety on denitrification is not critical for N removal in the Bardenpho process because it achieves efficient

N removal with respect to the other N removal process (i.e. the MLE process) up to an effluent nitrate concentration of about 5-6 mgN/ℓ. However, the exclusion of a factor of safety on denitrification for the Phoredox process may have serious consequences because the discharge of any nitrate to the anaerobic reactor severely reduces the P removal obtainable in the process. The effect of denitrification efficiency on excess biological P removal is discussed in detail in Chapter 7.

6.3 When Complete Denitrification Cannot be Achieved

In the Bardenpho process, if it is found that complete denitrification cannot be obtained, (i.e. $N_{ne} > 0$ from Eq 6.24 for all valid a-recycle ratios at the specified s-recycle ratios) nitrate will be present in the effluent and f_{xdt} will be equal to f_{xdm}. Generally, if the objective is N removal only, the Bardenpho process will be appropriate only if N_{ne} is less than 5 to 7 mgN/ℓ; when $N_{ne} > 5$ to 7 mgN/ℓ, - which will usually be the case if the TKN/COD ratio > 0,10 mgN/mgCOD - the MLE process (Fig 6.4) will yield a better nitrogen removal efficiency for the particular wastewater.

For the selected sludge age (R_s), factor of safety on nitrification (S_f) and wastewater characteristics (S_{ti}, N_{ti}, f_{bs}, T_{min}, T_{max}, f_{up}, f_{us}), the f_{xm} (Eq 5.24), N_c (Eq 5.29), f_{xdm} (Eq 6.23) and D_{pp} (Eq 6.25 with $f_{x1} = f_{xdm}$) for the MLE process are equal to those of the Bardenpho process and are found by the identical procedure (i.e. steps 1 to 8 given above). For the MLE process, the best denitrification performance is obtained when the anoxic reactor is just loaded with nitrate to its denitrification potential. For a specified s-recycle ratio, the mixed liquor a-recycle ratio which loads the anoxic reactor to its denitrification potential is the optimum a-recycle ratio, a_o, and will yield the minimum effluent nitrate concentration. When the nitrate load imposed on the anoxic reactor by the a- and s-recycles (including D.O. concentrations in the a- and s-recycles of O_a and O_s mgO/ℓ respectively), is less than or equal to the denitrification potential (D_{pp}), the nitrate concentration in the outflow of the anoxic reactor

is zero and that in the aerobic reactor and effluent is $N_c/(a+s+1)$ i.e. the nitrification capacity "diluted" into the total flow entering the aerobic reactor. Equating the nitrate load on the anoxic reactor imposed by the a- and s-recycles (including the D.O. in the recycles) to the denitrification potential D_{pp} and solving for the a-recycle ratio yields a_o;

$$a_o = \{-B + \sqrt{(B^2 + 4AC)}\}/(2A) \qquad (6.30)$$

where $A = O_a/2,86$

$$B = N_c - D_{pp} + \{(s+1)O_a + s.O_s\}/2,86$$

$$C = (s+1)(D_{pp} - sO_s/2,86) - sN_c$$

The effluent nitrate concentration N_{ne} for any a-recycle ratio less than or equal to a_o is given by Eq (6.31) but will be a minimum when $a = a_o$, i.e.

$$N_{ne} = N_c/(a + s + 1) \text{ mgN/}\ell \qquad (6.31)$$

In the design of an MLE process, it will be found the lower N_c is with respect to D_{pp} (i.e. the lower the influent TKN/COD ratio) the lower the N_{ne} and the higher the a_o. In practice, to operate an MLE process with an a_o-recycle ratio greater than 6:1 will be uneconomical: the increase in nitrate removal by increasing a_o from 6 to 10 is only 5% and, therefore, will not be cost-effective with respect to the increased pumping costs. Hence, the N removal of the MLE process is restricted by a maximum a-recycle ratio of say 6, which results in a minimum N_{ne} of 5 to 7 mgN/ℓ. This restriction on the MLE process will not be a problem in practice because high a_o are only obtained for wastewaters with low TKN/COD ratios (< 0,10 mgN/mgCOD) and these wastewaters are more effectively treated in a Bardenpho process (see section above). Alternatively, if near-complete or complete N removal is not essential, the sludge age can be reduced; for a fixed TKN/COD ratio this reduces D_{pp} (because f_{xm} is reduced) with respect to N_c and hence reduces a_o. The optimum R_s for the fixed TKN/COD ratio can be found using the

procedure set out above with different choices of R_s or, alternatively, the method of van Haandel, Dold and Marais (1982) can be used.

The design procedure for N removal processes set out above will be demonstrated in the next section with the aid of worked examples.

7. DESIGN EXAMPLES

The design of biological N removal plant by means of the procedure set out above is demonstrated by continuing the numerical example given in Chapter 4, Section 12 (in which the design procedure for organic material removal was demonstrated) and Chapter 5, Section 6 (in which the behaviour of nitrification was demonstrated).

7.1 Variability of Wastewater Characteristics

7.1.1 Variability of Nitrification Rate

The nitrification rate, as expressed by the maximum specific growth rate of the nitrifiers at 20°C (μ_{nm20}) is strongly dependent on the nature and source of the wastewater, so much so that it is considered a wastewater characteristic. The value can range from 0,65/d in purely domestic wastewaters down to 0,20/d for wastewaters with a large industrial* contribution. Owing to uncertainty in the μ_{nm20} value for a particular wastewater, in the absence of any data on the μ_{nm20} value, a low value, say between 0,3 to 0,4/d, needs to be selected to provide reasonable assurance that a safe design with respect to nitrification will be obtained
see Chapter 5, Section 4.1). In this design example, a value of 0,36/d is selected to demonstrate the situation in a design with a relatively low μ_{nm20} value (see Tables 6.1 and 6.2).

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*the type of industry referred to here is that which produces effluents which inhibit biological activity, e.g. metal finishing industry, plating works, paint production plants etc.

7.1.2 Variability in Denitrification Rates

The denitrification rates K at 20°C are relatively insensitive to the nature and source of the wastewater. However, different values have been observed with different wastewaters - in instances where the wastewater contains an appreciable industrial* contribution, reduced denitrification rates may be encountered. The denitrification rates used in this design example are the mean values found in the experimental work at the University of Cape Town, i.e. K_{120} = 0,720, K_{220} = 0,101 and K_{320} = 0,072 $mgNO_3$-N/(mgVASS.d) (see Table 6.2). These values were found on Strandfontein wastewater, which is an approximately average wastewater with a relative small industrial contribution. For most normal municipal wastewaters encountered in South Africa the denitrification rates given above are likely to result in a sufficiently accurate estimate of the denitrification potential of the process. Where there is doubt regarding the applicability of these rates, it is recommended that they are reduced by a factor of safety on denitrification, i.e. by about 1,1 to 1,2 times. The magnitude of the factor of safety should reflect the uncertainty in the applicability of the average denitrification rates given in this monograph.

7.1.3 Variability in Readily Biodegradable COD Fraction

The readily biodegradable COD fraction of a wastewater can vary considerably depending on the composition and origin of the various contributions that make up the wastewater. It has been found that in approximately normal principally domestic raw wastewater, approximately 20% of the total (or 25% of the biodegradable) COD is readily biodegradable. However, where industrial wastewaters containing a high biodegradable organic material content are discharged to the municipal sewerage system, significantly higher

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*Industries producing biodegradable wastes e.g. malting factories, breweries, fruit and vegetable processing factories, etc. do not fall in this group as these may *promote* biological N and P removal. (see Section 7.1.3).

readily biodegradable COD fractions can be encountered. For example, yeast factories, breweries, malting processes and fruit and vegetable juicing and canning industries produce wastewaters with high readily biodegradable COD fractions. Municipal wastewaters containing contributions from these sources can have relatively high readily biodegradable COD fractions depending on the magnitude of the industrial discharges.

Many factors can reduce the readily biodegradable COD fraction of a wastewater. For example the discharge of waste biological sludge to the sewerage system for sludge handling at treatment works lower down the sewer line can deplete a wastewater of all the readily biodegradable COD, particularly if the combined flow is lifted by Archimedian screw pumps. Further examples are cited in Chapter 3, Section 3.2.

The above examples demonstrate that the readily biodegradable COD fraction can differ significantly between different wastewaters. Consequently, it is recommended that whenever possible, the fraction should be measured. The importance of this fraction in biological nitrogen (and phosphorus) removal is such that it is always worth the effort of measuring it.*

It should be noted that the readily biodegradable COD fraction (as defined by Eqs 2.8 and 2.9) is affected by primary sedimentation. This is because primary sedimentation removes a large fraction of the particulate COD but very little soluble COD. Consequently, the readily biodegradable COD concentrations (S_{bsi}) are approximately the same before and after primary sedimentation but, because the total or biodegradable COD (S_{ti}, S_{bi}) has been significantly reduced in the primary settlers, the readily biodegradable COD fraction (f_{ts}, f_{bs}) of the settled wastewater is increased (see Chapter 2, Section 2).

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*The readily biodegradable COD fraction f_{ts} (or f_{bs}) or the actual concentration S_{bsi} cannot be measured directly. Its measurement requires the operation and monitoring of a single completely mixed activated sludge process at a very short sludge age under daily cyclic square wave loading conditions (see Appendix 2).

For the design example it will be assumed that the readily biodegradable COD fraction with respect to the biodegradable COD f_{bs} for the raw wastewater is 0,24, i.e. the value found for approximately normal principally domestic raw wastewaters. The readily biodegradable COD fraction (f_{bs}) of the settled wastewater assuming that primary sedimentation removes 40% of the total COD but only 10% of the readily biodegradable COD is 0,33. (see Table 6.1 Chapter 4, Section 12.1 and Chapter 2, Section 2).

Table 6.1 Raw and settled wastewater characteristics important for denitrification (for other characteristics see Tables 4.3 and 5.2)

Parameter	Symbol	Value		Units
		Raw	Settled	
Maximum specific growth Rate of Nitrifiers at 20°C	μ_{nm20}	0,36	0,36	/d
Denitrification rates at 20°C	K_1	0,720	0,720	$mgNO_3$-N/
	K_2	0,101	0,101	mgVASS/
	K_3	0,072	0,072	d.
Readily Biodegradable COD fraction	f_{bs}	0,24	0,33*	

*Note increase on f_{bs} fraction in settled wastewater (see Section 7.1.3) - based on a 40% total COD decrease and a 10% readily biodegradable COD decrease in the primary settling tanks. (See Chapter 4, Section 12.1 and Table 4.3).

7.2 Effect of Temperature

From the kinetics of denitrification discussed above, it is clear that the denitrification rates K_1, K_2 and K_3 all decrease with decreasing temperature. This, combined with the fact that the maximum specific growth rate of the nitrifiers at 20°C (μ_{nm20}) also decreases with decreasing temperature has the result that the critical condition for the nitrogen removal process is the average *minimum* wastewater temperature. The design completed for the average minimum wastewater temperature (T_{min}) is checked at the average maximum wastewater temperature (T_{max}) because the oxygen demand per unit COD load increases as the temperature increases.

To facilitate the calculations of the design example at T_{min} = 14°C and T_{max} = 22°C, the denitrification rates K_1, K_2 and K_3 are adjusted for temperature in Table 6.2. Temperature adjustment of μ_{nm20} and b_n is given in Table 5.3, but for convenience is repeated in Table 6.2.

Table 6.2 Temperature adjustment of the denitrification rates K_1, K_2 and K_3

Constant	Symbol	20°C	θ	14°C	22°C	Eq.No.
1st Denit.rate in Prim.Anoxic	K_{120} *	0,720	1,200	0,241	1,036	6.12
2nd Denit.rate in Prim.Anoxic	K_{220} *	0,101	1,080	0,0636	0,1178	6.13
Denit.rate in Second Anoxic	K_{320} *	0,072	1,029	0,0607	0,0762	6.10
Max.Spec.growth rate of Nitrifiers	μ_{nm20} †	0,36	1,123	0,18	0,45	5.13
Endog.Resp.rate for Nitrifiers	b_{n20} †	0,04	1,029	0,034	0,042	5.14

* Units: $mgNO_3$-N/(mgVASS.d)

† Units: per d.

7.3 Maximum Unaerated Sludge Mass Fraction

This aspect is discussed in detail in Chapter 5, Section 4.4 but it is briefly repeated here because sizing of the maximum unaerated sludge mass fraction is one of the most important decisions in the design of a nutrient removal process.

For nitrogen removal processes, the larger the unaerated sludge mass fraction (f_{xt}) the greater the nitrogen removal and the lower the effluent nitrate concentration. Generally at a minimum temperature of 14°C, to obtain an f_{xt} of 0,50 for favourable μ_{nm20} values (0,40/d), a sludge age of 15 to 20 days is required to ensure nitrification (S_f = 1,25) (see Eq 5.24); for less favourable μ_{nm20} values (between 0,3 and 0,4/d), the required sludge age is 20 to 30 days (see Fig 6.14). Now because the volume of the process is directly proportional to the mass of sludge in it (see Chapter 4, Section 6) a 30 day sludge age process will require a process volume about 1/3 larger than a 20 day one. Consequently, for unfavourable μ_{nm20} values it may be preferable to accept a lower f_{xm} and a higher effluent nitrate concentration - a reduction of f_{xm} from 0,50 at R_s = 30 days to f_{xm} = 0,40 at R_s = 22 days results in a 30% saving in process volume and an increase in effluent nitrate concentration of 6 mgN/ℓ (for an influent COD of 600 mg/ℓ and TKN/COD ratio of 0,10). The above argument applies also to favourable μ_{nm20} values because, depending on the effluent quality requirements, it may be acceptable to design a 15 day sludge age process with an effluent nitrate concentration of 5 mgN/ℓ rather than a 20 day process which can achieve complete denitrification (depending on the TKN/COD ratio). Also, for instances where both the μ_{nm20} and TKN/COD ratio are unfavourable, a 20 day sludge age process with external energy source addition, to augment denitrification, may be a more economical process than a 35 day process. *Clearly, the decision on the unaerated sludge mass fraction and sludge age of the process should not be taken too lightly, because with these two parameters fixed, the N removal of the process with the influent and self-generated energy sources is fixed, so that with fixed influent wastewater characteristics, the effluent quality will be fixed (see Chapter 3).*

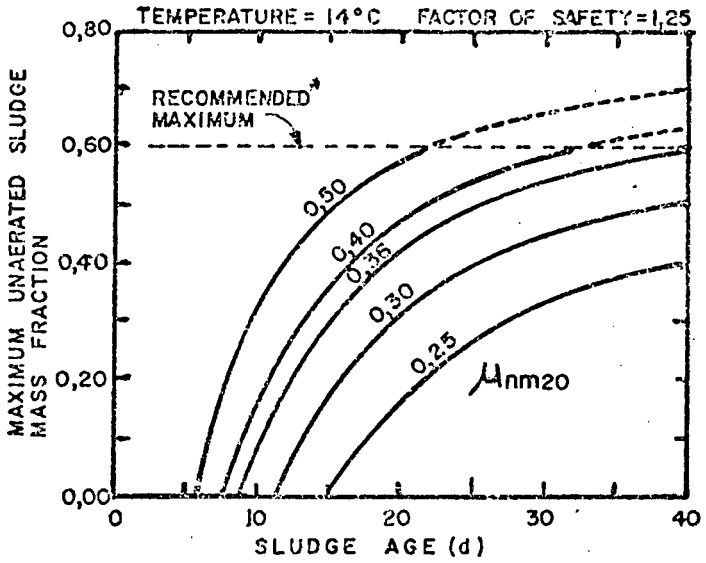

Fig 6.14 *Maximum unaerated sludge mass fraction versus sludge age for different maximum specific growth rates of the nitrifiers at 20°C (μ_{nm20}) at 14°C and factor of safety (S_f) of 1,25. (From Eq 5.24).*

For the wastewater characteristics of the design example i.e. T = 14°C and μ_{nm20} = 0,36/d (see Tables 4.3 and 5.2) and accepting a factor of safety on nitrification S_f = 1,25, a 25 day sludge age process is required for f_{xm} = 0,50 (see Chapter 5, Section 4.4 and Fig 6.14). As this sludge age is not excessively long for f_{xm} = 0,50, a 25 day sludge age process will be accepted for a preliminary design analysis.

7.4 Nitrification

Because a factor of safety of 1,25 was imposed in the design of the unaerated sludge mass fraction and sludge age, the minimum sludge age for nitrification is sufficiently below the actual sludge age to assure that complete nitrification will take place i.e. the effluent TKN concentration can be assumed to be 3 mgN/ℓ. (see Chapter 5, Section 4.4). This can be checked by repeating the

nitrification calculations given in Chapter 5 for 25 days sludge age.

For the raw wastewater characteristics (i.e. f_{up} = 0,13 mgCOD/mgCOD, f_{us} = 0,05 mgCOD/mgCOD, T_{min} = 14°C, S_{ti} = 600 mgCOD/ℓ - see Tables 4.3 and 5.2) and 25 days sludge age, and accepting the nitrogen content of the volatile solids f_n to be 0,10 mgN/mgVSS, the nitrogen required for sludge production is given by Eq (4.23) i.e.

$$N_s = 600.0,10 \left[\frac{0,45\ (1 - 0,05 - 0,13)}{(1 + 0,20.25)}\ (1 + 0,2.0,20.25) + \frac{0,13}{1,48} \right]$$

$$= 600.0,021 = 12,6 \text{ mgN/ℓ}.$$

The nitrification capacity (N_c) is found from Eq (5.29) i.e. for the raw wastewater at 14°C

$$N_c = 48 - 12,6 - 3 = 32,4 \text{ mgN/ℓ}.$$

The nitrification oxygen demand is found from Eq (5.39) i.e.

$$M(O_n) = 4,57.\ N_c.\ Q$$

$$= 4,57.\ 32,4.\ 13,33.\ 10^6 \text{ mgO/d}$$

$$= 1973 \text{ kgO/d}.$$

The above calculations for N_s, N_c and $M(O_n)$, including those for the raw wastewater at 22°C and the settled wastewater at 14°C and 22°C, are tabulated in Table 6.3.

In the design, because it is intended to reduce the nitrate concentration as much as possible, the Alkalinity change in the wastewater will be minimized: Assuming that 80% of the nitrate formed is denitrified, the alkalinity change $\Delta Alk = 7,14.N_c - 3,57.$ (Nitrate denitrified) $= -7,14.\ 32,4 + 3,57.\ 0,80.\ 32,4 = -139$ mg/ℓ as $CaCO_3$.

With an influent Alk of 200 mg/ℓ as $CaCO_3$ (see Table 5.2) the effluent Alk = 200 - 139 = 61 mg/ℓ as $CaCO_3$, which, from Fig 5.6, will maintain a pH above 7, (see Chapter 5, Section 4.3).

7.5 Denitrification

Accepting a sludge age of 25 days, which allows a maximum unaerated sludge mass fraction f_{xm} of 0,50, the denitrification behaviour of the Bardenpho and MLE processes will be demonstrated for the typical raw and settled wastewaters at 14°C and 22°C.

In the calculations it will be assumed that there is a dissolved oxygen concentration of 2 mgO/ℓ in the interconnecting flows from the aerobic to the anoxic reactors (i.e. O_a = 2 mgO/ℓ) and 1 mgO/ℓ in the underflow recycle from the secondary settling tank (i.e. O_s = 1 mgO/ℓ). The underflow recycle ratio (s) is assumed to be 1:1.*

For nitrogen removal processes, the maximum anoxic sludge mass fraction (f_{xdm}) is equal to the maximum unaerated sludge mass fraction (f_{xm}) i.e. f_{xdm} = 0,50 (see Eq 6.23). The denitrification potential of the primary anoxic reactor at 14°C with $f_{x1} = f_{xdm}$ = 0,50 for the raw wastewater is found from Eq (6.20) (see Eq 6.25)

$$D_{pp} = (1-0,05-0,13)\ 600\{\frac{0,24\ (1-0,45.1,48)}{2,86} +$$

$$0,0636.0,50.0,45.25/(1+0,20.25)\}$$

$$= 492(0,028+0,0596)$$

$$= 13,8 + 29,3$$

$$= 43,1 \text{ mgN}/\ell.$$

*This is usually fixed at a value such that satisfactory settling tank operation is obtained. Secondary settling tank behaviour is described in Chapter 8.

The D_{pp} values for the raw wastewater at 22°C and those for the settled wastewater at 14°C and 22°C are listed in Table 6.3.

The minimum primary and secondary anoxic sludge mass fractions (f_{x1min} and f_{x3min}) are found from Eq (6.21) and Eq (6.29) respectively. For example for the raw wastewater at 14°C,

$$f_{x1min} = \frac{0,24(1-0,45.1,48)(1+0,20.25)}{2,86.0,241.0,45.25}$$

$$= 0,062 \qquad \text{and}$$

$$f_{x3min} = \frac{(1+1)2,0(1+0,20.25)}{(1-0,05-0,13)600.0,45.25.0,0607.2,86}$$

$$= 0,025$$

The values for the raw wastewater at 22°C and those for the settled wastewater at 14°C and 22°C are given in Table 6.3.

At this stage of the design procedure, we have collected all the information necessary to check whether or not complete denitrification can be achieved i.e. steps 1 to 11 of the step by step procedure have been completed.

Continuing the procedure with step 12, a value for the a-recycle ratio is selected and the effluent nitrate concentration is calculated from Eq (6.24). Selecting a = 3,3 then for the *raw wastewater at 14°C*,

$$N_{ne} = \frac{\{\frac{32,4}{3,3+1+1} + \frac{2}{2,86}\}\{3,3 + \frac{0,0636}{0,0607}(1+1)\} + \frac{1.1}{2,86} - 43,1}{\{\frac{0,0636}{0,0607} + 1(\frac{0,0636}{0,0607} - 1)\}}$$

$$= -5,47 \text{ mgN}/\ell$$

Because $N_{ne} < 0,0$, N_{ne} must be set equal to zero. Setting $N_{ne} = 0$ and substituting into Eqs (6.26 to 28) yields the optimum primary (f_{x1}),

Table 6.3 Summary of design calculations for the Bardenpho and MLE processes treating raw or settled wastewater at 25 days sludge age. Wastewater characteristics given in Tables 4.3, 5.2 and 6.1.

Parameter	Symbol	Units	Raw Wastewater				Settled Wastewater			
			Bardenpho		MLE		Bardenpho		MLE	
Temperature	T	°C	14	22	14	22	14	22	14	22
Safety factor	S_f		1,25	2,7	1,25	2,7	1,25	2,7	1,25	2,7
Max.unaerated sludge mass	f_{xm}		0,50	0,50	0,50	0,50	0,50	0,50	0,50	0,50
Effluent TKN	N_{te}	mgN/ℓ	3,0	2,0	3,0	2,0	3,0	2,0	3,0	2,0
N for sludge production	N_s	mgN/ℓ	12,6	12,0	12,6	12,0	5,7	5,4	5,7	5,4
Nitrification capacity	N_c	mgN/ℓ	32,4	34,0	32,4	34,0	32,3	33,6	32,3	33,6
Nitrif.oxygen demand	$M(O_n)$	kgO/d	1973	2071	1973	2071	1961	2046	1961	2046
Max. anoxic sludge mass	f_{xdm}		0,50	0,50	0,50	0,50	0,50	0,50	0,50	0,50
Max. denit. potential	D_{pp}	mgN/ℓ	43,1	58,7	43,1	58,7	31,1	41,2	31,1	41,2
D.O. in a-recycle	O_a	mgO/ℓ	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0
D.O. in s-recycle	O_s	mgN/ℓ	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0
Underflow recycle ratio	s		1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0
Min.Prim. anoxic	f_{x1min}		0,062	0,017	-	-	0,085	0,029	-	-
Min.Sec. anoxic	f_{x3min}		0,024	0,023	-	-	0,039	0,036	-	-
Optimum a-recycle ratio	a_o		3,3	5,0	17,2*	36,0*	2,2	5,0	4,7	13,4*
Effluent nitrate	N_{ne}	mgN/ℓ	0,0	0,0	1,7*	0,9*	4,9	1,7	4,8	2,2*
Prim. anoxic	f_{x1}		0,16	0,16	0,50	0,50	0,30	0,30	0,50	0,50
Sec. anoxic	f_{x3}		0,24	0,19	-	-	0,20	0,20	-	-
Total anoxic	f_{xdt}		0,40	0,35	0,50	0,50	0,50	0,50	0,50	0,50

* These are the theoretical results from Eqs (6.30 and 6.31). Owing to an economical upper limit to the mixed liquor a-recycle ratio, these theoretical a_o values should not be implemented in practise. (see text).

secondary (f_{x3}) and total (f_{xdt}) anoxic sludge mass fractions *just* to achieve complete denitrification with an a-recycle ratio of 3,3 i.e.

$$f_{x1} = \frac{\{\frac{32,4}{3,3+1+1} + \frac{2}{2,86}\}\ 3,3 + (0+\frac{1}{2,86})\ 1 - \frac{0,24.0,334.492}{2,86}}{492\ \frac{0,45.25}{(1+0,20.25)}\ 0.0636}$$

$$= 0,16$$

$$f_{x3} = \frac{\{(1+1)[\frac{32,4}{3,3+1+1} + \frac{2}{2,86} - 0]\ \frac{0,0636}{0,0607}\}}{492\ \frac{0,45.25}{1+0,20.25}\ 0,0636}$$

$$= 0,24$$

$$f_{xdt} = 0,40$$

The above calculation is repeated for different values of a. The results of N_{ne}, f_{x1}, f_{x3} and f_{xdt} are shown plotted versus a in Fig 6.15a. Repeating the design procedure *at 22°C* (steps 12 to 15) for the raw wastewater produces the results shown in Fig 6.15b (see also Table 6.3).

Figure 6.15 shows that, *for the raw wastewater*, complete denitrification can be achieved at *14°C* for any a-recycle ratio > 1,8 (Fig 6.15a). At *22°C* (Fig 6.15b), a minimum f_{xdt}* for complete denitrification of 0,35 occurs at a = 5,0. The f_{x1} corresponding to a = 5,0 is 0,16 and this fixes the design value of f_{x1} for both 14°C and 22°C. Now if f_{x3} is fixed at 22°C at the value corresponding to f_{x1} i.e. f_{x3} = 0,19 (Fig 6.15b), then f_{xdt} will be insufficient to achieve complete denitrification at 14°C; for a fixed f_{x1}, f_{xdt} at 14°C is

*If T_{max} is less than 18°C, a clear minimum cannot be discerned (see Fig 6.15a at 14°C). In this event, any reasonable f_{x1} can be selected with the proviso that complete utilization of the readily biodegradable COD can be assured even with a significant decrease in K_{120} (see Eqs 6.12 and 6.21). The existence of a minimum, and the temperature above which it becomes discernable, depends much on the choice of the D.O. concentrations in the recycles, O_a and O_s.

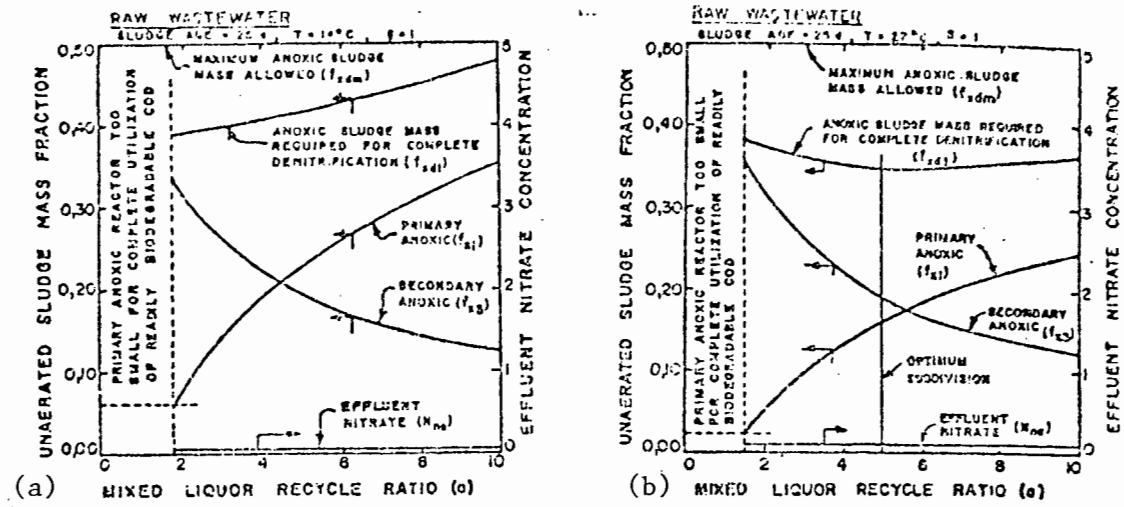

Fig 6.15 *Primary (f_{x1}), secondary (f_{x3}), total (f_{xdt}) and maximum allowable (f_{xdm}) anoxic sludge mass fractions and effluent nitrate concentrations (N_{ne}) versus mixed liquor a-recycle ratio for the Bardenpho process treating raw wastewater at 25 days sludge age at 14°C (left Fig 6.15a) and 22°C (right Fig 6.15b).*

greater than f_{xdt} at 22°C (compare Figs 6.15a and b). Hence f_{x3} is fixed at 14°C at the value corresponding to f_{x1} = 0,16 i.e. f_{x3} = 0,24 (Fig 6.15a). Hence f_{xdt} = 0,40 for complete denitrification at 14°C and 22°C.

With f_{x1} and f_{x3} fixed for both 14°C and 22°C, the optimum performance of the process is achieved when it is operated at the a-recycle ratio corresponding to the fixed f_{x1} value, this a-recycle ratio being the optimum a_o; at 14°C, a_o = 3,3 (Fig 6.15a) and for 22°C, a_o = 5,0 (Fig 6.15b). This demonstrates that as the temperature increases, the a-recycle ratio needs to be increased to maintain optimum performance. This is because with increase in temperature, the denitrification potential of the primary anoxic reactor (D_{p1}) increases and consequently more nitrate must be recycled to it to fully utilize its D_{p1}. It should be noted that with f_{x1} and f_{x3} fixed, the use of any a-recycle ratio other than a_o results in

poorer denitrification performance: if $a < a_o$, D_{p1} is not fully utilized and if $a > a_o$, unnecessarily large quantities of D.O. are discharged to the primary anoxic reactor.

The design parameters calculated above are summarized in Table 6.3.

The design procedure *for the settled wastewater* at *14°C and 22°C* was repeated and the results are shown plotted in Figs 6.16a and b respectively. At 22°C (Fig 6.16b), a minimum effluent nitrate concentration* of 1,7 mgN/ℓ is obtained with a = 5,0. The f_{x1} corresponding to a = 5,0 is 0,30 and this value fixes f_{x1}. Now because the maximum anoxic sludge mass fraction is fully utilized i.e. $f_{xdt} = f_{xdm}$, f_{x3} is fixed at the difference between f_{xdm} and f_{x1} i.e. $f_{x3} = 0,20$. Hence f_{x1} and f_{x3} are fixed at 0,30 and 0,20 respectively for 14°C and 22°C. The optimum a-recycle ratio is 5,0 at 22°C yielding an effluent nitrate concentration of 1,7 mgN/ℓ and that at 14°C is 2,2 (i.e. the value corresponding to $f_{x1} = 0,30$, Fig 6.16a) yielding $N_{ne} = 4,9$ mgN/ℓ. The design results are listed in Table 6.3.

The design calculations above show that with the *raw wastewater*, complete denitrification can be obtained and is achieved with a total anoxic sludge mass fraction (f_{xdt}) of 0,40 whereas 0,50 is allowed (f_{xdm}). As N removal only is important in this example, the Bardenpho process is appropriate and (i) if a factor of safety for complete denitrification is required, either option 1 (see Section 6 above) can be taken i.e. f_{x1} and f_{x3} are increased such that $f_{x1} + f_{x3} = f_{xdt} = f_{xm} = 0,50$ or (ii) if no factor of safety for complete denitrification is required, option 2 can be taken i.e. the sludge age can be reduced such that $f_{xm} = f_{xdt} = 0,40$.

For the *settled wastewater*, complete denitrification cannot be achieved at both 14°C and 22°C. Because the maximum anoxic sludge mass fraction is fully utilized (i.e. $f_{xdt} = f_{xdm} = 0,50$), the

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*see footnote on Page 6.49, but refer to Fig 6.16b.

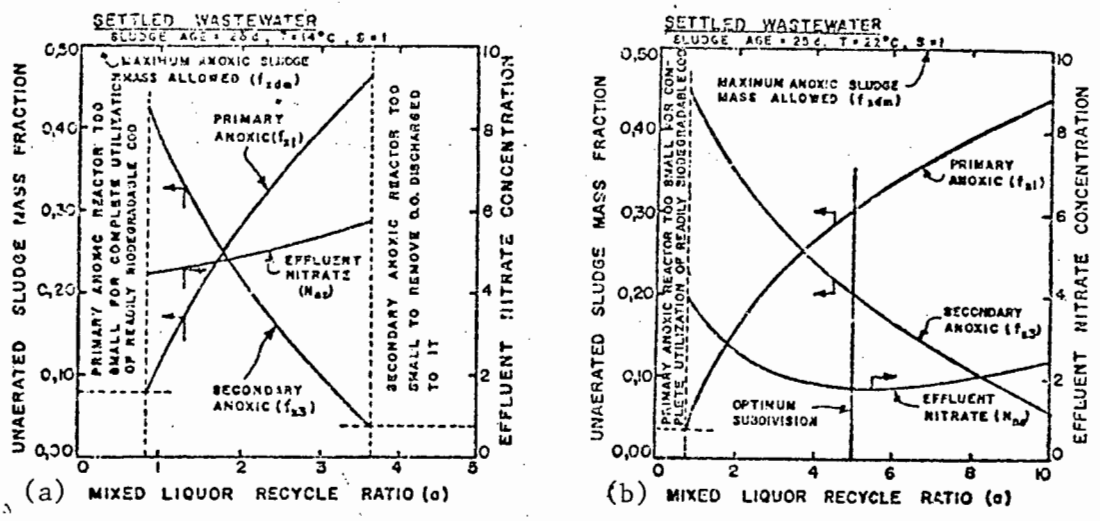

Fig 6.16 *Primary (f_{x1}), secondary (f_{x3}), total (f_{xdt}) and maximum allowable (f_{xdm}) anoxic sludge mass fractions and effluent nitrate concentration (N_{ne}) for the Bardenpho process treating settled wastewater at 25 days sludge age at 14°C (left, Fig 6.16a) and 22°C (right, Fig 6.16b).*

denitrification efficiency can be improved only by increasing the sludge age of the process. However, the increase in sludge age is at the expense of an increased process volume. A sludge age of 40 days, which allows $f_{xm} = f_{xdm} = 0{,}60$*, is required to produce complete denitrification at 14°C (found by trial and error using design procedure). From Eq (4.21) an increase in sludge age from 25 to 40 days represents an increase in process volume of about 40%. Such a large increase in volume may not merited for an improvement in effluent nitrate concentration from 5 to 0 mgN/ℓ. Consequently a sludge age of 25 to 30 days is considered the maximum economical sludge age beyond which there is little cost effective improvement in denitrification efficiency. If complete denitrification must be achieved, it may be preferable to treat raw wastewater at 20 days sludge age which allows an f_{xdm}

*This is the recommended upper limit for the maximum unaerated sludge mass fraction (see Chapter 5, Section 4.4).

= f_{xm} = 0,40 (see Fig 6.15a). Although this increases the process volume by 80% it removes the problem of primary sludge disposal. Alternatively, when treating settled wastewater, and complete denitrification must be achieved, a 20 day sludge age process with readily biodegradable COD addition to the primary or secondary anoxic reactor may be economically viable - if 60* mgCOD per litre influent readily biodegradable COD is added to the plant, complete denitrification will be obtained with settled wastewater at 14°C and 20 days sludge age. For the design flow of 13,3 Mℓ/d, the COD addition is 60.13,3 = 800 kg/d i.e. 10% of the raw wastewater COD load.

If complete denitrification is not essential, the Bardenpho process as designed for the settled wastewater i.e. sludge age = 25 days, is appropriate. Alternatively, the feasibility of an MLE process can be checked to see whether or not this process may yield a more economical design. The design procedure for the MLE process is demonstrated below.

The design procedure for the MLE process is identical to that for the Bardenpho process up to step 9 of the step by step procedure. For the same design conditions of the Bardenpho process (i.e. R_s = 25 days etc), the results for the MLE process are listed in Table 6.3 and can be seen to be identical to those of the Bardenpho process. Substituting the values for the nitrification capacity N_c and denitrification potential D_{pp} into Eqs (6.30 and 6.31), the optimum mixed liquor a-recycle ratio a_o and minimum effluent nitrate concentration N_{ne} are obtained; e.g. for the *settled wastewater at 14°C* -

A = 2/2,86 = 0,70

B = 32,3-31,1 + {(1+1)2 + 1.1}/2,86 = + 2,95

C = (1+1)(31,1 - 1.1/2,86) - 1.32,3 = + 29,2

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*Assuming that N_{ne} = 7,0 mgN/ℓ at R_s = 20 days (i.e. 2 mgN/ℓ greater than at R_s = 25 days), the COD consumption for its removal is 7,0.8,6 = 60 mgCOD/ℓ influent.

Hence

$$a_o = \{-2,95 + \sqrt{2,95^2 + 4.0,70.29,2}\}/(2.0,70)$$

$$= 4,7 \quad \text{and}$$

$$N_{ne} = 32,3/(4,7 + 1+1) = 4,8 \text{ mgN}/\ell.$$

The above results, as well as those for the settled wastewater at 22°C and those for the raw wastewater at 14°C and 22°C are listed in Table 6.3.

The results show that for all cases except one (i.e. for settled wastewater at 14°C), the optimum mixed liquor a-recycle ratio a_o exceeds 5. Although these results include the discharge of dissolved oxygen to the anoxic reactor, recycle ratios above 4 to 5 are not cost effective - the small decrease in effluent nitrate concentration (N_{ne}) which an increase in a-recycle ratio from 5 to 10 produces does not warrant the additional pumping costs (e.g. for $N_c = 33$, $N_{ne} = 4,7$ for $a = 5$ and 2,7 for $a = 10$). Consequently, the a-recycle ratio is limited at 5, which results in a minimum N_{ne} from the MLE process of about 5 to 6 mgN/ℓ for most municipal wastewaters. Hence for N removal processes, if effluent nitrate concentrations lower than 5 to 6 mgN/ℓ are required, the Bardenpho process is the indicated process because this process can achieve low N_{ne} with low a-recycle ratios.

Comparing the Bardenpho and MLE processes, (see Table 6.3) if the effluent quality standards require that complete or near complete denitrification must be produced, then the Bardenpho process is the more superior process for both the raw and settled wastewaters. However the process needs to be operated at a sludge age of about 20 days for the *raw wastewater* yielding complete denitrification) and at least 30 days for the *settled wastewater* (yielding an effluent nitrate concentration of about 3 mgN/ℓ) - the settled wastewater process will have a smaller volume than the raw wastewater process but will have the additional problem of primary sludge

disposal. Alternatively, if complete denitrification is not necessary and an effluent nitrate concentration of 5 to 6 mgN/ℓ is acceptable, the MLE process will be an acceptable process. For the raw wastewater, a sludge age of only 15 days (yielding f_{xm} = f_{xdm} = 0,32) is sufficient to produce an effluent nitrate concentration of about 5 mgN/ℓ with the MLE process and for the settled wastewater, a sludge age of 25 days will yield an effluent nitrate concentration of about 5 mgN/ℓ.

7.6 Process Volume and Oxygen Demand

7.6.1 Process Volume

Having determined the subdivision of the sludge mass into anoxic and aerobic fractions to achieve the required nitrogen removal, the actual sludge mass in the process needs to be calculated to determine the volumes of the different reactors. The mass of total (MLSS) or volatile (MLVSS) sludge in the activated sludge process for a selected sludge age and wastewater characteristics is given by Eq (4.21) (see Chapter 4, Section 4) i.e. for the given raw and settled wastewater characteristics, the MLSS sludge mass in the process at 25 days sludge age and 14°C is 54200 and 21850 kgTSS respectively. Selecting an MLSS concentration in the process of 4000 mg/ℓ* (i.e. 4 kg/m³), the volume of the process treating raw wastewater is 13550 m³ and that treating settled wastewater is 5460 m³. Now, because the sludge mass in the nitrogen removal processes is uniformly distributed in the process, i.e. each reactor has the same MLSS concentration, the volume fractions of the reactors are equal to the sludge mass fractions. Accepting the Bardenpho process design for the raw and settled wastewaters (see Table 6.3) the volume of the reactors are found directly from the sludge mass fraction and total process volumes; reactor retention times, nominal and actual are found from the reactor volumes and the nominal and total flows passing through them - see Table 6.4. Note that the reactor nominal retention time is a consequence of the mass of sludge

*A method for estimating the reactor MLSS concentration for design condition is as follows: for a selected X_t calculate the process volume requirements. For accepted settling characteristics of the sludge, calculate the required settler surface area for the selected X_t (see Chapter 8). Estimate the com bined cost of the process and settling tanks. It will be found that as X_t increases the cost of the process decreases but the cost of the settling tan increases. The X_t that gives the minimum combined cost is the indicated ML concentration (usually between 3000 and 6000 mgTSS/ℓ with settled wastewater being lower than raw wastewater).

Table 6.4 Reactor volumes, nominal and actual retention times for the Bardenpho process treating the typical raw and settled wastewater at 25 days sludge age. For process performance see Table 6.3.

Process Parameter	Symbol	Raw Wastewater	Settled Wastewater	Units
Sludge mass	$M X_t$	54200	21850	kgTSS
MLSS concentration	X_t	4000	4000	mg/ℓ
Total volume	V_p	13550	5460	m³
Total flow	Q	13330	13330	m³/d
Total nom.retention	R_{nt}	24,4	9,8	hr
Mixed liq.recycle (14°C)	a	3,3	2,2	
Und. recycle	s	1,0	1,0	
Primary anoxic				
Mass fraction	f_{x1}	0,20	0,30	
Volume		2710	1640	m³
Nom.ret.time		4,9	2,9	h
Actual ret.time		1,13	0,92	h
Main aeration				
Mass fraction*		0,45	0,45	
Volume		6100	2460	m³
Nom.ret.time		11,0	4,4	h
Actual ret.time		2,6	1,4	h
Secondary anoxic				
Mass fraction	f_{x3}	0,30	0,20	
Volume		4060	1090	m³
Nom.ret.time		7,3	2,0	h
Actual ret.time		3,7	1,0	h
Reaeration				
Mass fraction*		0,05	0,05	
Volume		680	270	m³
Nom.ret.time		1,2	0,50	h
Actual ret.time		0,6	0,25	h

*The reaeration reactor is usually taken to have a sludge mass fraction of around 0,05 to 0,07 and this fraction is deducted from the aerobic sludge mass fraction; the remaining aerobic sludge mass fraction constitutes the main aeration sludge mass fraction.

generated from the influent COD load, the selected MLSS concentration and the sludge mass fraction - the retention time *per se* has no significance in kinetics of nitrification and denitrification (see Chapter 4, Sections 6 and 12).

7.6.2 Daily Average Total Oxygen Demand

The total oxygen demand in a nitrogen removal process is the sum of that required for carbonaceous material (COD) degradation and nitrification, less than recovered by denitrification. The daily average oxygen demand for (i) carbonaceous material removal (MO_c) is given by Eq (4.15) (see Chapter 4, Section 7), and (ii) nitrification is given by Eq (5.39) (see Section 7.4 above and Chapter 5, Section 6.5) and these oxygen demands in the Bardenpho process at 25 days sludge age for the typical raw and settled wastewaters at 14°C and 22°C are listed in Table 6.5.

The oxygen recovered by denitrification (MO_d) is given by 2,86 times the nitrate mass denitrified (see Section 1.3) where nitrate mass denitrified is the product of the daily average influent flow Q and the nitrate concentration denitrified. The nitrate concentration denitrified is given by the difference in the nitrification capacity N_c and the effluent nitrate concentration: Hence

$$M(O_d) = 2,86.(N_c - N_{ne})Q \qquad (6.32)$$

From the denitrification performance data of the Bardenpho process in Table 6.3, the oxygen recovered by denitrification for the typical raw and settled wastewaters are listed in Table 6.5.

For the raw wastewater, Table 6.5 shows that (i) the nitrification oxygen demand (MO_n) is about 40% that required for COD removal (MO_c), (ii) about 60% of MO_n can be recovered by incorporating denitrification, (iii) the additional oxygen demand by incorporating nitrification and denitrification is only 15% of that required for COD removal only and (iv) the effect of temperature on the total oxygen demand is marginal - less than 3% (see also Fig 6.1).

Table 6.5 Daily average oxygen demand (in kgO/d) in the 25 day sludge age Bardenpho process for the typical raw and settled wastewaters at 14°C and 22°C

Oxygen Demand kgO/d	Symbol	Raw		Settled	
		14°C	22°C	14°C	22°C
1. Carbonaceous*	$M(O_c)$	+5105	+5205	+3287	+3352
2. Nitrification**	$M(O_n)$	+1973	+2071	+1961	+2046
3. Denitrification***	$M(O_d)$	-1235	-1296	-1048	-1216
4. Total	$M(O_t)$	+5843	+5980	+4200	+4185

* See Chapter 4, Section 12.3, Eq (4.27)

** See Section 7.4 above

*** From Eq (6.32) and Table 6.3

For the settled wastewater, Table 6.5 shows that (i) the nitrification oxygen demand is about 60% of that required for COD removal, (ii) about 50% of the nitrification oxygen demand can be recovered by denitrification, (iii) the additional oxygen demand by incorporating nitrification and denitrification is about 30% of that required for COD removal only and (iv) the effect of temperature on the total oxygen demand is marginal - less than 3% more at the lower temperature.

Comparing the oxygen demand for the raw and settled wastewaters, it can be seen that the total oxygen demand for the latter is about 30% less than that of the former. This saving is possible because primary sedimentation removes 35 to 45% of the raw wastewater COD (see Chapter 4, Section 12 and Chapter 5, Section 6.5). Furthermore for the settled wastewater, the nitrification oxygen demand is a greater proportion of the total, and also, less of the nitrification oxygen demand can be recovered by denitrification compared to the raw wastewater. These effects are due to the higher TKN/COD ratio of the settled wastewater.

Generally for design, preliminary estimates of the total daily average oxygen demand can be roughly approximated with the following:

i) including complete nitrification;

$$M(O_t) = \{1 + 5\ f_{ns}\}\ M(O_c) \qquad (6.33)$$

ii) including complete nitrification, and denitrification to the degree possible depending on the TKN/COD ratio (see Fig 6.17)

$$M(O_t) = \{1 + 2\ f_{ns}\}\ M(O_c) \qquad (6.34a)$$

for $f_{ns} < 0{,}09$ (i.e. effluent nitrate < 2 mgN/ℓ)

$$= \{1 + 2\ f_{ns}\ [1+10(f_{ns}-0{,}08)]\}M(O_c) \qquad (6.34b)$$

for $f_{ns} > 0{,}09$ (i.e. effluent nitrate > 2 mgN/ℓ)

where f_{ns} = influent TKN/COD ratio.

These equations, in conjunction with the carbonaceous oxygen demand $M(O_c)$ equation in terms of the influent COD load (MS_{ti}) (see Chapter 4, Section 7) will allow the calculation of preliminary estimates of the daily average total oxygen demand in nitrogen removal processes between sludge ages of 15 to 30 days for raw and settled wastewaters for known influent COD loads and TKN/COD ratios.

Knowing the average daily total oxygen demand, the peak total oxygen demand can be roughly estimated by means of a simple design rule. From a large number of simulations with the general dynamic model, it was found that provided the factor of safety on nitrification (S_f) is greater than 1,25 to 1,35, the relative amplitude {i.e. (Peak-Average)/Average} of the total oxygen demand is a fraction 0,50 of the relative amplitude of the total oxygen demand potential of the influent COD and TKN load {i.e. $Q(S_{ti} + 4,57.N_{ti})$}. For example, with the raw wastewater design, if the peak influent total oxygen demand potential is obtained at a time of day when the influent flow rate, COD and TKN concentrations are 23,1 Mℓ/d, 863 mgCOD/ℓ and 65 mgN/ℓ respectively - i.e. 23,1 (863 + 4,57.65) = 26800 kgO/d - and the average total oxygen demand potential is 13,33 (600 + 4,57.48= = 10920 kgO/d (see Table 4.3), the relative amplitude of the total influent oxygen demand potential is (26800 - 10920)/10920 = 1,45; hence the relative amplitude of the total oxygen demand is approximately 0,50.1,45 = 0,72; from Table 6.5 the average daily total oxygen demand is 5980 kgO/d (at 22°C) and hence the peak oxygen demand is 1,72.5980 = 10300 kgO/d. As with all simplified design rules, the above rule should be used with discretion and caution, and where possible, the peak total oxygen demand is best estimated by means of the general dynamic activated sludge model.

7.7 Closure

In the above design example, the raw wastewater TKN/COD ratio is 0,08 mgN/mgCOD. If the calculations are repeated for the raw wastewater but assuming different TKN/COD ratios and sludge ages, it will be found that (i) for a fixed sludge age, once the TKN/COD ratio is above that with which complete denitrification can be achieved, the

effluent nitrate concentration increases as the TKN/COD ratio increases and (2) at a fixed TKN/COD ratio above that with which complete denitrification can be achieved, as the sludge age increases, the effluent nitrate concentration decreases. This implies that at a fixed sludge age, the N removal potential of the process is fixed so that the effluent quality depends on the magnitude of the influent TKN/COD ratio; however the N removal potential of the process may be improved by increasing the sludge age.

Based on 14°C and the raw wastewater characteristics of the design example (except the TKN/COD ratio) the behaviour described above is shown graphically in Fig 6.17, in which the influent TKN/COD ratio is plotted versus the effluent nitrate concentration that can be achieved at different sludge ages. The process volume required at the different sludge ages (as a fraction of that required at 25 days)

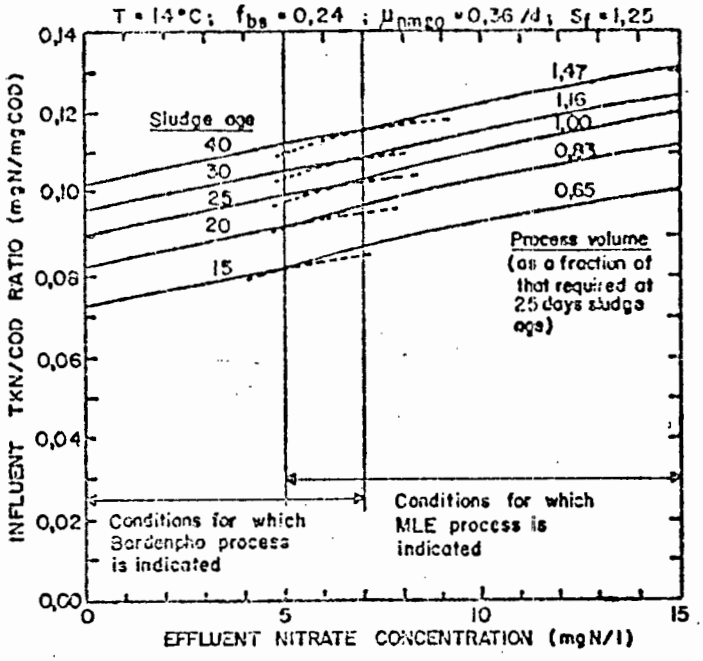

Fig 6.17 *Effluent nitrate concentration attainable for different influent TKN/COD ratios for N removal processes operating at different sludge ages for T = 14°C, readily biodegradable COD fraction (f_{bs}) = 0,24 and maximum specific growth rate of the nitrifiers at 20°C (μ_{nm20}) = 0,36/d*

is also given on Fig 6.17. The areas for which the Bardenpho and MLE process achieve the optimum N removal are demarcated and generally where the effluent nitrate concentration is greater than 5 to 6 mgN/ℓ, the MLE process will yield an improved efficient nitrate concentration at an economical mixed liquor a recycle ratio i.e. < 4:1. It should be noted that at a fixed TKN/COD ratio, the total average daily oxygen demand does not vary significantly between different sludge ages so that aeration costs do not significantly affect the conclusions that can be drawn from Fig 6.17 (see Fig 6.1).

Figure 6.17 shows that for a TKN/COD ratio of say 0,095 mgN/mgCOD, complete denitrification can be achieved if the sludge age is 30 days in a Bardenpho process. However, if an effluent quality of 7 mgN/ℓ is acceptable, then this can be achieved in an MLE process at a sludge age of 20 days. The process volume saving that can be made by reducing the effluent nitrate standard from 0 to 6 mgN/ℓ is 1-0,93/1,16 = 0,28 i.e. the MLE process at 20 days sludge age with 7 mgN/ℓ is about 30% smaller than the Bardenpho process at 30 days sludge age with complete denitrification. Figure 6.17 shows also that for low μ_{nm20} values, 14°C and 25 days sludge age (to avoid excessively large process volumes), the Bardenpho process can achieve (i) complete denitrification for TKN/COD ratios less than 0,090 mgN/mgCOD; (ii) near complete denitrification (i.e. effluent nitrate concentration between 1 and 5 mgN/ℓ) for TKN/COD ratios between 0,09 and 0,10 mgN/mgCOD and (iii) incomplete denitrification (i.e. effluent nitrate concentration above 5 mgN/ℓ) for TKN/COD ratios above 0,10 mgN/mgCOD; hence the MLE process is the indicated process for TKN/COD ratios above 0,10. The above limits are relatively sensitive to the μ_{nm20} value and readily biodegradable COD fraction; (i) the limits are given for a low μ_{nm20} value (around 0,36/d) because this will be the usual case in design unless sufficient information is available justifying the use of a higher one (see Appendix 3) - if μ_{nm20} is greater than 0,40/d, the results will be simila to those shown in Fig 6.17 except that they can be achieved at shorter sludge ages; (ii) the limits given are for an approximately normal raw wastewater readily biodegradable COD fraction f_{bs} of 0,24 - there are many factors which can affect the f_{bs} fraction of a wastewater (see Section 7.1.3 above) so that at the design stage, the value of f_{bs} also will

be uncertain [unless the value has been measured (see Appendix 2)] and it is likely that a value of 0,24 will be used initially for want of a better estimate; if the actual f_{bs} value is greater than 0,24, lower effluent nitrate concentrations will be obtained than those given in Fig 6.17 and if f_{bs} is lower than 0,24, higher effluent nitrate concentrations will be obtained.

Although the limits given in Fig 6.17 should not be taken as general because of their dependence on the wastewater characteristics, in particular μ_{nm20} and f_{bs}, they are useful for setting approximate guidelines for N removal process selection and the sludge age at which it is to be operated to achieve a certain effluent nitrate concentration for a given influent TKN/COD ratio. The guidelines in Fig 6.17 are not intended to obviate doing detailed design calculations but serve the purpose of demonstrating the behaviour of N removal processes. Indeed it is recommended that in process design, the wastewater characteristics are changed to encompass a range of possible values for the particular wastewater and to undertake design calculation for combinations of different wastewater characteristics. This will allow the selection of a process design that can best deal with anticipated changes in wastewater characteristics and will expose weaknesses in the design so that control measures can be incorporated to deal with fluctuations in wastewater characteristics during the life of the plant.

8. REFERENCES

1. Arkley M and G v R Marais (1982) Effect of the anoxic sludge mass fraction on the activated sludge process. Research Report No W 38, Dept. of Civil Eng., Univ. of Cape Town.
2. Barnard J L (1973) Biological denitrification, Wat.Pollut.Control, 72, 6, 705-720.
3. Carlson D E (1971) Nitrogen removal and identification for water quality control, OWRR, Project No 4040, Dept. of Civil Eng., Univ. of Washington.
4. Chang J P and J E Morris (1962) Studies of the utilization of nitrate by *Miaococcus Denitrificans*, J.Gen.Microbial., 29, 301.
5. Christensen M H and P Harremoës (1977) Biological denitrification of sewage: A literature review. Prog.Wat.Tech., 8, 415, 509-555.
6. Dold P L, G A Ekama and G v R Marais (1980) A general model for the activated sludge process. Prog.Wat.Tech., 12, 47-77.

7. Ekama G A and G v R Marais (1978) The dynamic behaviour of the activated sludge process. Research Report No W 27, Dept. of Civil Eng., Univ. of Cape Town.

8. Ekama G A, A C van Haandel and G v R Marais (1979) The present status of research on nitrogen removal: a model for the modified activated sludge process. Presented at the Symposium on Nutrient Removal, S A Branch of IWPC Pretoria, May 1979. Proceedings published by Water Research Commission of South Africa.

9. Ludzack F J and M B Ettinger (1962) Controlling operation to minimize activated sludge effluent nitrogen, JWPCF, 34, 920-931.

10. Marsden M G and G v R Marais (1977). The rôle of the primary anoxic reactor in denitrification and biological phosphorus removal. Research Report No W 19, Dept. of Civil Eng., Univ. of Cape Town.

11. Siebritz I P, G A Ekama and G v R Marais (1980) Excess Biological Phosphorus removal in the Activated Sludge Process at Warm Temperate Climates. Proc. Waste Treatment and Utilization, Vol.2, 233-251, Eds. C W Robinson, M Moo-Young and G J Farquhar, Pergamon Press, Toronto.

12. Stern L B and G v R Marais (1974) Sewage as the electron donor in biological denitrification. Research Report No W 7, Dept. of Civil Eng., Univ. of Cape Town.

13. van Haandel A C, G A Ekama and G v R Marais (1981) The activated sludge process part 3 - single sludge denitriirication. Water Research, 15, 1135-1152.

14. van Haandel and Marais (1981) Nitrification and denitrification kinetics in the activated sludge process. Research Report No W 39, Dept. of Civil Eng., Univ. of Cape Town.

15. van Haandel A C, P L Dold and G v R Marais (1982) Optimization of nitrogen removal in the single sludge activated sludge process. Presented at 11th IAWPR Conf. Cape Town. To be published in Water, Science and Technology.

16. Wilson D E and G v R Marais (1976) Adsorption phase in biological denitrification. Research Report No W 11, Dept. of Civil Eng., Univ. of Cape Town.

17. Wuhrmann K (1964) Nitrogen removal in sewage treatment processes, Vehr.Int.Ver.Theor.Angew.Lumnol, 15, (in German).

CHAPTER SEVEN

BIOLOGICAL EXCESS PHOSPHORUS REMOVAL

by

G A Ekama, G v R Marais and I P Siebritz

1. INTRODUCTION

From the first publication reporting phosphorus removal in excess of normal metabolis requirements in some activated sludge plants there has been controversy as to the mechanism whereby the excess P removal is accomplished, whether the mechanism is a precipitation of inorganic compounds, albeit biologically mediated, or biological through metabolic formation and accumulation of phosphorus compounds in or on the organisms. The objective of this chapter is not to discuss the evidence that supports the excess biological P removal hypothesis*, but to describe briefly the theory of biological excess P removal as understood by the authors and to demonstrate how this theory can be used as an aid for the design of biological P removal activated sludge processes. This does not imply that precipitation of inorganic phosphorus salts due to chemical changes resulting from biological action e.g. alkalinity, acidity and pH does not take place:** Such inorganic precipitation certainly can take place, but it would appear that in the treatment of municipal wastewaters by an appropriately designed activated sludge process, within the normal ranges of pH, alkalinity, acidity and calcium concentrations in the influent, excess P removal is principally mediated by a biological mechanism.

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* For a review of the observations that support the biological excess P removal hypothesis, see Marais, Loewenthal and Siebritz (1982).

** Points of view with regard to biological mediated precipitation of phosphorus are presented in the Post Conference Seminar on Phosphate Removal in Biological Treatment Process, IAWPR, Pretoria (1982).

2. BACKGROUND

2.1 Earlier Developments

From the reports of the earlier investigators into excess biological P removal (e.g. Fuhs and Min Chen, 1975 and Barnard, 1976), one conclusion emerged which now appears to be generally accepted: excess P removal is stimulated by stressing the organisms by withholding the oxygen supply. Quantification of this stress, however, presented major problems *and still does*, because the parameters in terms of which the stress is to be formulated are not yet explicitly identified.

Barnard (1976) from pilot scale studies (Barnard, 1975a and b) on the Bardenpho process (Fig 7.1) reported that excess biological P removal is induced if at some point in the process configuration the organism mass is stressed by subjecting it to an "anaerobic"* state (i.e. a state in which neither oxygen nor nitrate is present) such that phosphorus is released by the sludge mass to the bulk liquid. He proposed to produce this stage efficiently by including an anaerobic reactor ahead of the primary anoxic reactor in the Bardenpho process, this reactor receiving the influent flow and the underflow recycle from the secondary settling tanks, (Fig 7.2). This configuration has become known in South Africa as the 5-stage Phoredox or simply the Phoredox process, and in the United States as the Modified Bardenpho process.

To explain the excess removal phenomenon, Barnard in 1976 hypothesized that it is not the release *per se* that stimulates the excess uptake mechanism but that the release indicates that a certain low redox potential has been established, i.e. that the low redox potential triggers off the release and thereby stimulates excess P

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*Anoxic; anaerobic: The meaning we will attach to these two terms, in nitrification-denitrification processes, follows that originally used by Barnard, i.e. Anoxic: a state in which nitrate is present but no oxygen; Anaerobic: a state in which neither nitrate nor oxygen is present. The inadequacies of these definitions is apparent when attempting to compare the state of two reactors of the same size in a completely mixed and a plug flow reactor respectively. A completely mixed anaerobic reactor, for example, will have no nitrate in the reactor and effluent; the equivalent plug flow reactor however may contain nitrate for a considerable portion of the reactor length i.e. be partly "anoxic", partly "anaerobic" - the inadequacy arises in that no indication is given as to the *intensity* of the state.

uptake. In terms of this hypothesis nitrate recycled via the underflow to the anaerobic reactor will restrain, in some degree, the level to which the redox potential can be lowered and consequently, nitrate can be expected to influence excess P uptake adversely. No data on redox potential was reported. Barnard apparently accepted that the Bardenpho section of the plant should reduce the nitrate sufficiently that any nitrate in the underflow would not prevent the attainment of the low redox potential necessary for P release in the anaerobic reactor. In any event he considered that nitrate entering the anaerobic reactor could be countered by increasing the retention time of this reactor. For design of the anaerobic reactor he suggested a nominal retention time of one hour, Barnard (1976).

Barnard's work on the nitrification-denitrification excess P removal process stimulated extensive research into this process, to gain experience on its behaviour, to delineate more precisely the factors influencing excess removal and to develop criteria for design. Nicholls (1975) at full scale, and McLaren and Wood (1976) and Simpkins and McLaren (1978) at laboratory and pilot scale applied the Phoredox process at approximately 20°C to treat effluents from Johannesburg and Pretoria, and were successful in attaining excess P removal. They were also successful in obtaining excess P removal in the 3-stage Phoredox (Fig 7.3) i.e. a Phoredox process without the secondary anoxic and reaeration reactors. Simpkins and McLaren found that (1) the anaerobic reactor was necessary for excess P removal, (2) nitrate in the recycle adversely affected P removal and (3) increasing the volume of the anaerobic reactor increased the excess P removal. These findings were in conformity with Barnard's redox potential hypothesis although again no redox potential measurements were reported.

None of the investigations above provided a reliable model to predict the magnitude of the denitrification to be expected even though it was evident that for design, evaluation of the nitrate in the recycle could be crucial in assessing the success of a process both in stimulation of the P release and magnitude of the P uptake.

Marais and his group (Stern 1974, Martin 1975, Marsden 1976, Wilson 1976 with Marais) recognized the importance of quantifying the nitrate removal. To obtain information on the magnitude and kinetics of denitrification they replaced the completely mixed reactors in the Bardenpho process by plug flow reactors and measured the nitrate along the reactor axes under constant flow and load conditions. At the same time they also monitored the phosphate behaviour in the various reactors making up the processes. Their findings on denitrification kinetics are reviewed in Chapter 6. With regard to the phosphorous behaviour with the raw sewage they used as influent difficulties were experienced in obtaining nitrification, even at long sludge ages of 10 to 20 days, if the unaerated mass fraction of the sludge exceeded 30 to 40%. When the plants were operated at unaerated mass fractions that allowed nitrification the denitrification obtained was insufficient and the effluent nitrate was high. Yet these plants gave very good phosphorus removal. However when the sewage source was changed the good P removal previously obtained declined virtually to zero.

In a subsequent study of the Phoredox process, Rabinowitz and Marais (1980) selected the 3-stage Phoredox (Fig 7.3) as the basic configuration in preference to the 5-stage for the following reason: The wastewater source did not allow an unaerated mass reaction of greater than 40 percent at 14°C for a sludge age (R_s) of 20 days if efficient nitrification was to be maintained; taking account of the fact that in the Phoredox process the anaerobic reactor cannot contribute to the process denitrification potential, the 5-stage process could not reduce the nitrate to zero for the measured TKN/COD ratio of the waste flow. Consequently (as discussed earlier in Chapter 6) the secondary anoxic reactor volume was added to the primary anoxic to obtain the maximum nitrate removal and hence the minimum nitrate concentration in the underflow recycle. The findings from this investigation can be summarized as follows:

(1) When the nitrate concentration in the effluent (and underflow recycle) was low usually P release and excess uptake were observed. In general there was a tendency for the excess uptake to decrease quite disproportionately as the nitrate in

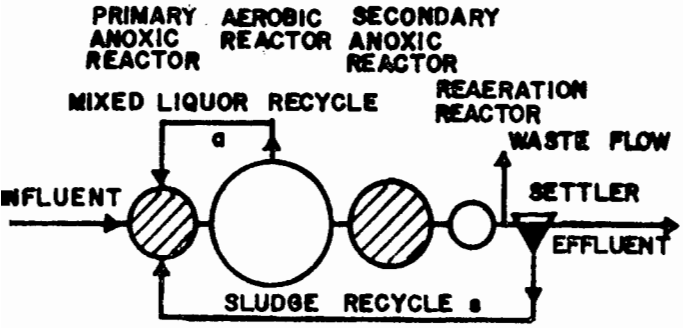

Fig 7.1 *The Bardenpho process for biological nitrogen removal.*

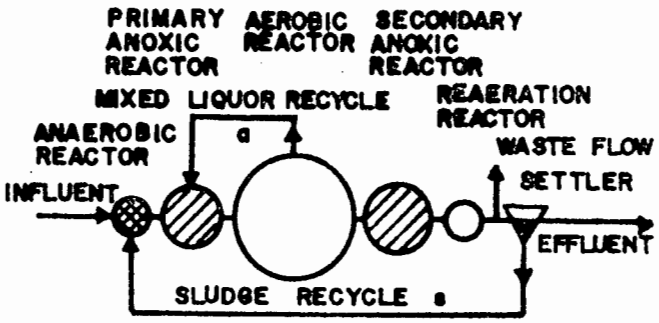

Fig 7.2 *The Phoredox process for biological nitrogen and phosphorus removal, also called the Modified Bardenpho process.*

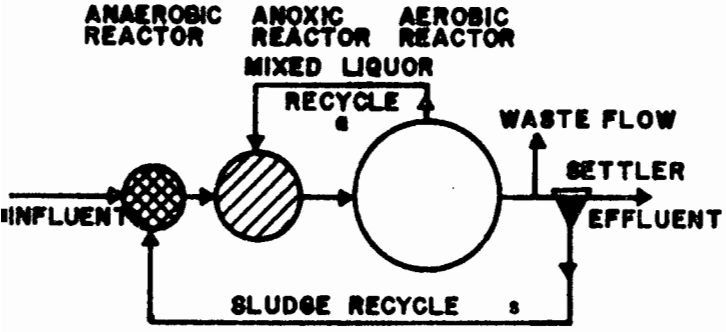

Fig 7.3 *The 3 stage Phoredox process for biological nitrogen and phosphorus removal.*

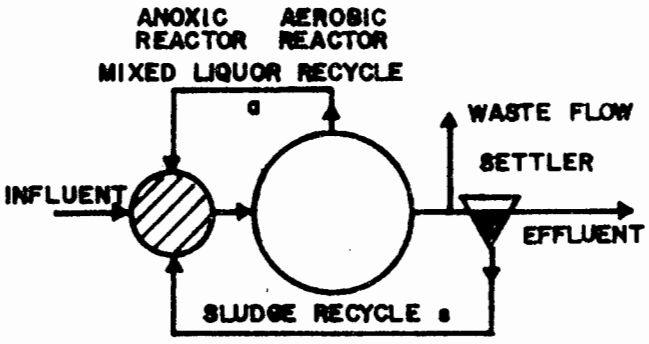

Fig 7.4 *The modified Ludzack-Ettinger process for biological nitrogen removal.*

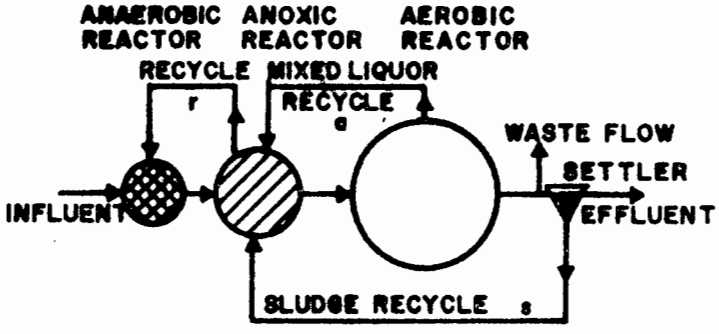

Fig 7.5 *The UCT process for biological nitrogen and phosphorus removal.*

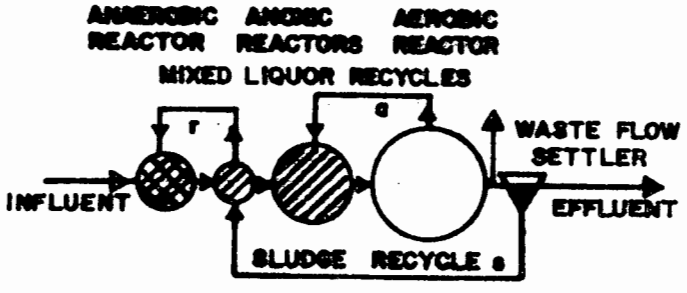

Fig 7.6 *The modified UCT process for biological nitrogen and phosphorus removal.*

the recycle increased, a behaviour also noted by Simpkins and McLaren, and Barnard.

(2) With different batches of wastewater having the *same* nitrate concentration in the recycle, one batch may give high P release and excess removal whereas the next may give no (or little) release and little excess removal. No apparent reason for this behaviour could be discovered.

The overall P removal performance was disappointing; not only did the plant not remove P in excess over long periods of time but the removal was erratic due to the effects of (1) or (3) above, or all. Increasing the anaerobic mass fraction during periods of low P removal was found to be counter-productive as this could be done only at the expense of the *anoxic* mass fraction which in turn gave rise to increased nitrate in the recycle. It was finally concluded that for the waste flows used in the experimental investigation, treatment by the Phoredox type process was not suitable for excess P removal; this did not imply that the process might not be suitable for other waste flows but the investigation did bring to light that there were constraints, not adequately recognized before, that may prevent high P removals:

(1) For any selected sludge age and minimum temperature the requirement for efficient nitrification imposes an upper limit on the unaerated mass fraction.

(2) The limitation on the unaerated mass fraction correspondingly limits the concentration of nitrate that can be removed. If the nitrate generated is higher than the denitrification achievable, nitrate will appear in the effluent and, in the Phoredox system, the P removal will be adversely affected.

2.2 Later Developments

2.2.1 Positive Exclusion of Nitrate from the Anaerobic Reactor

From the findings on the Phoredox process the Marais group concluded that irrespective of other factors that may affect the excess P uptake, a major factor influencing the uptake was the

presence of nitrate in the underflow recycle. If the nitrate content in the underflow to the reactor could be kept at low concentration, then there was a high expectation that excess P removal would be obtained. The principal obstacle to attaining this desirable end in the Phoredox process appeared to be that the nitrate discharged to the anaerobic reactor is linked directly to the concentration in the effluent. If for any reason the nitrate concentration increased while the COD remained constant, i.e. if the influent TKN/COD ratio increased, the process appeared to offer little option to reduce this by operational means. The only operational means available was to reduce the magnitude of the underflow recycle but this was a risky option as the settleability of the mixed liquor in the plants tended to be poorer than in pure aerobic systems. Evidently a process configuration was needed that made the anaerobic reactor *independent* of the effluent nitrate concentration. Towards this end, after a series of attempts, the configuration shown in Fig 7.5 was devised called the University of Cape Town process (UCT process).

In the UCT process, the settling tank underflow s-recycle as well as the mixed liquor a-recycle are discharged to the anoxic reactor and an additional mixed liquor r-recycle from the anoxic to the anaerobic reactor is introduced. The nitrate recycled to the anoxic reactor can be controlled by appropriately adjusting the mixed liquor a-recycle such that the nitrate concentration in the outflow of the anoxic reactor remains approximately zero. Consequently the mixed liquor r-recycle from the anoxic to the anaerobic reactor will contain very little or no nitrate and the anaerobic condition in the anaerobic reactor will be optimal. Thus, *in the UCT process by application of an appropriate operational control strategy, the anaerobic reactor can be maintained independent of the nitrate in the effluent even if the influent TKN/COD ratio to the plant varies.*

Laboratory scale tests on the UCT process using waste flows from Cape Town showed improved excess P removal in both the concentration removed and consistency in removal over those obtained in the Phoredox process. But perhaps the most important achievement

from a research point of view, was that with the UCT process it was possible to eliminate the confounding effect of the nitrate in the recycle flow to the anaerobic reactor on excess P removal so that other factors influencing the excess removal could be investigated with greater ease. In the experimental response data the effects of these other factors became clearly evident:

(1) For the same influent COD, one batch of sewage gave high removals, another gave low, an observation previously surmised but not explicitly identified due to the difficulty of isolating this effect when nitrate was recycled to the anaerobic reactor.

(2) Generally as the storage time of a batch of sewage (at 5°C) increased, both the excess P removal and the nitrate removal declined. Evidently on storage a progressive change was taking place in the constitution of the sewage which acted adversely on the two phenomena; direct evidence of change was indicated by the gradual reduction of COD of the batch during storage.

2.2.2 Phosphorus Removal Process Analyses

Owing to the importance attached to the nitrate concentration discharged to the anaerobic reactor in excess biological P removal, the nitrogen removal theory was applied to the P removal processes to investigate their propensity for removing nitrogen.

(i) The Phoredox Process: In this process, a certain fraction (f_{xa}) of the total unaerated sludge mass fraction (f_{xt}) is "set aside" as an anaerobic reactor to establish the prerequisites for excess phosphorus removal. Only the remaining unaerated sludge mass fraction ($f_{xdt} = f_{xt} - f_{xa}$) is available as primary and secondary anoxic reactors for nitrogen removal. If no nitrate is to be recycled to the anaerobic reactor (to ensure the most "intense" anaerobic condition) complete denitrification must be achieved in the anoxic sludge mass fraction (f_{xdt}). The denitrification behaviour of the anoxic reactors in the Phoredox process for complete denitrification is the same as those in the Bardenpho process for complete denitrification. However, due to the presence of the anaerobic reactor (f_{xa}), the anoxic sludge mass fraction (f_{xdt}) for

the Phoredox process ($f_{xdt} = f_{xt} - f_{xa}$) is less than that for the Bardenpho process ($f_{xdt} = f_{xt}$). Hence, the upper limit of the TKN/COD ratio for complete denitrification in the Phoredox process is lower than that for complete denitrification in the Bardenpho process, by about 0,005, for approximately normal municipal wastewaters with f_{xa} = 0,15 at 14°C. Consequently, for an unsettled "normal" municipal wastewater, at 25 days sludge age and 14°C, the 5 stage Phoredox process will achieve complete denitrification only if the TKN/COD ratio is less than about 0,085*. Should the TKN/COD ratio exceed this limit, complete denitrification is unlikely resulting in nitrate in the effluent and underflow s-recycle. From a design point of view, to provide a factor of safety, the TKN/COD ratio limit should not exceed 0,07* to 0,08* at 14°C, for sludge age 20 to 30 days, to have reasonable assurance that complete denitrification will be attained. The safe upper limit, of a 0,07 to 0,08 TKN/COD ratio, for successful implementation of the Phoredox process, restricts application of the process in the treatment of municipal wastewaters because the TKN/COD ratio of raw wastewater ranges between 0,07* and 0,09* and that of settled wastewater generally is above 0,10*.

(ii) The UCT Process: The analysis of the UCT process (Fig 7.5) showed that also for this process, there is also an upper TKN/COD ratio above which excess P removal is unlikely to be attained. For a normal municipal wastewater at a TKN/COD of 0,14* (at 14°C and 25 days sludge age) the nitrate concentration in the effluent and hence in the underflow s-recycle is so high that this recycle by itself (at s = 1) fully loads the anoxic reactor to its denitrification potential i.e. the mixed liquor a-recycle needs to be reduced to zero. Hence, for TKN/COD ratios > 0,14, nitrate will be present in the primary anoxic reactor and a discharge of nitrate to the anaerobic reactor cannot be avoided leading to a decline in excess P removal. For design, to introduce a factor of safety on the denitrification, the upper limit for the TKN/COD ratio above which excess P removal is

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*These limits apply to a readily biodegradable COD fraction f_{ts} = 0,20 (f_{bs} = 0,24). For higher (lower) f_{ts} fractions these limits are higher (lower). It should be noted that throughout this monograph, where TKN/COD ratio limits are given, these apply for f_{ts} = 0,20 (f_{bs} ≅ 0,24) unless otherwise stated.

unlikely to be attained in the UCT process is 0,12 to 0,14. This limit is above that for most settled and raw municipal wastewaters.

(iii) The Modified UCT Process: Experience with the UCT process exposed two different types of problems that could significantly affect the successful operation of the process, these were (i) process control and (ii) sludge settleability.

(i) The mixed liquor a-recycle ratio needs to be carefully controlled so that the primary anoxic reactor is just underloaded with nitrate to avoid a nitrate discharge to the anaerobic reactor. Under full-scale operation such careful control of the a-recycle ratio is not possible due to uncertainty to the TKN/COD ratio, particularly under cyclic flow and load conditions. To simplify the operation of the UCT process a modification was sought whereby careful control of the a-recycle would not be necessary.

(ii) As the TKN/COD ratio increases, the a-recycle ratio needs to be decreased to avoid a nitrate discharge to the anaerobic reactor, this in turn causes an increase in the *actual anoxic retention time*. For relatively high influent COD concentrations (> 500 mgCOD/ℓ), and TKN/COD ratios > 0,11, the actual anoxic retention time exceeds one hour. From experimental observation, in some of the units, when the actual anoxic retention time exceeded 1 hour, the settleability of the sludge declined.* To preserve good settleability of the sludge, a modification to the UCT process was sought whereby the actual anoxic retention time could be limited at 1 hour.

Both problems above are associated with the a-recycle ratio; both problems can be accommodated by a modification of the UCT process called the Modified UCT process (Fig 7.6). In the Modified UCT process, the *anoxic* reactor is subdivided into two reactors, the

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*For reasons not yet understood the anaerobic retention time, both nominal and actual does *not* appear to affect the settleability of the sludge.

first having a sludge mass fraction of about 0,10 and the second having the balance of the anoxic sludge mass fraction available. The first anoxic reactor receives the underflow s-recycle and the r-recycle to the anaerobic reactor is taken from it. The second anoxic reactor receives the a-recycle. The minimum a-recycle is that which introduces just sufficient nitrate to the second anoxic reactor to load it to its denitrification potential. Any recycle higher than the minimum will not remove additional nitrate so that at higher recycles more nitrate is introduced than removed in the second anoxic reactor and nitrate will appear in the effluent from this reactor. This however is immaterial insofar as it affects the nitrate in the aerobic reactor which remains constant once $a > a_{min}$. Consequently one can raise the a-recycle to any value greater than a_{min}, to give the required actual retention time, without affecting the nitrate recycled to the first anoxic reactor - careful control of the a-recycle is no longer necessary. This improvement however is obtained at a cost: the maximum TKN/COD ratio to give a zero nitrate discharge to the anaerobic reactor is reduced from 0,14 in the UCT process to 0,11 in the Modified UCT process. However a TKN/COD ratio of 0,11 mgN/mgCOD includes most settled and raw municipal wastewaters. Furthermore, by making provision that the r-recycle can be taken from either the first or second anoxic reactor, the process can be operated either as a modified UCT or a UCT process, as may be required.

The developments described so far were all guided by the hypothesis that excess P removal is stimulated, and is best achieved, by having an anaerobic reactor and that it is optimized by preventing nitrate from entering the reactor. No information was available to quantify firstly, the conditions in the anaerobic reactor that cause the stimulation and, secondly, the magnitude of the excess P removal to be expected. Accordingly these two aspects were further investigated.

3. EVOLUTION OF EXCESS PHOSPHORUS REMOVAL MODEL

3.1 Prerequisite for Excess Phosphorus Removal

The improved understanding of the nitrogen removal process

behaviour led to a new approach in investigating the prerequisites in the anaerobic reactor for excess phosphorus removal. Ekama, van Haandel and Marais (1979) hypothesized that if the mass of nitrate entering an unaerated reactor is less than that reactor's denitrification potential, the difference defines an "*anaerobic capacity*" in the reactor. They speculated that this anaerobic capacity could substitute for the redox potential level (suggested by Barnard, 1976) as a measure for predicting when phosphorus release would take place in the anaerobic reactor. Siebritz, Ekama and Marais (1980) intensively investigated this hypothesis. They plotted the P release in the anaerobic reactor, the P uptake in the aerobic reactor and the system P removal versus the anaerobic capacity (A_c) for data from UCT and modified Phoredox processes (Fig 7.7). This plot shows that (i) if A_c < 10 mgNO_3-N/ℓ, no P release in the anaerobic reactor is obtained; in fact, P uptake is noted, (ii) when A_c > 10 mgNO_3-N/ℓ, P release is obtained, and (iii) as A_c increases

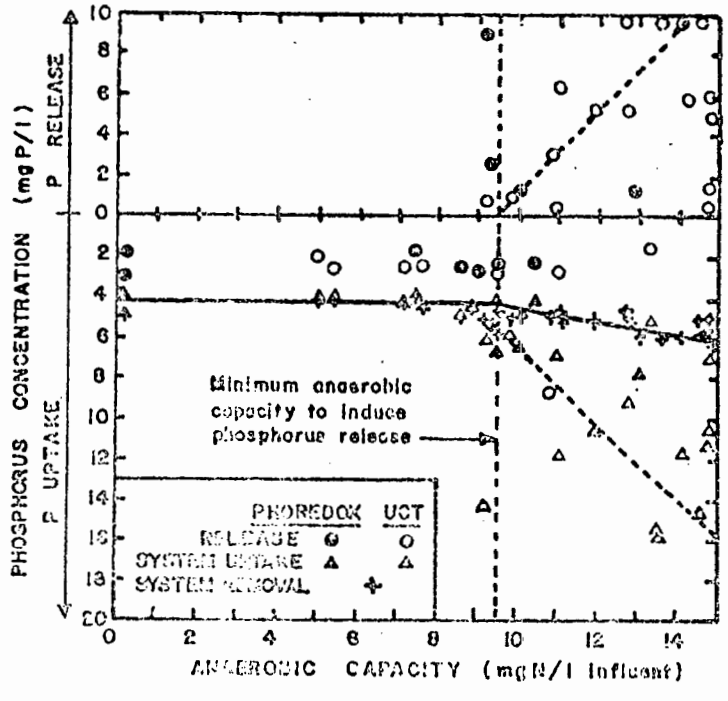

Fig 7.7 *P release in the anaerobic reactor, process P uptake and process P removal versus the anaerobic capacity of the anaerobic reactor (A_c) for the modified Phoredox and UCT processes.*

above 10 $mgNO_3$-N/ℓ so the P release in the anaerobic reactor, the P uptake in the aerobic reactor and the system P removal increase.*

The data in Fig 7.7 appeared to support the anaerobic capacity hypothesis. Consequently if the anaerobic hypothesis was correct, then provided this capacity could be induced in any system other than the UCT and Phoredox processes, P release and uptake should be observed.

To test the above conclusion experimentally, three Modified Ludzack-Ettinger (MLE) processes (Fig 7.4) and a modified UCT process were set up and fed from the same wastewater source. The three MLE units were given unaerated sludge mass fractions of 40, 55 and 70 percent respectively and the mixed liquor a-recycle ratios were set such that the anaerobic capacities ranged from 6 to 35 $mgNO_3$-N/ℓ in the anoxic reactors. Over two months of operation no P release nor excess P removal were observed in any of the MLE units. In contrast, the modified UCT process with a 0,10 anaerobic sludge mass fraction, consistently gave P release and excess P removal. It was concluded from these results that the anaerobic capacity hypothesis is not sustained.

In seeking an explanation for the different P release behavioural patterns in the modified UCT and MLE processes, it was noted that the only evident difference lay in the concentration of readily biodegradable COD surrounding the organisms in the anaerobic reactor (S_{bsa}). In the modified UCT process the readily biodegradable COD concentration in the anaerobic reactor (S_{bsa}) is the maximum possible as no nitrate is recycled to the anaerobic reactor; in contrast, in the MLE process sufficient nitrate is recycled to the anoxic reactor to utilize all the readily biodegradable COD i.e. $S_{bsa} = 0,0$. Therefore the different behavioural patterns of the processes would be consistently described if it was assumed that the concentration of readily biodegradable COD in

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*From Fig 7.7 (and Fig 7.8) it can be seen that having stimulated P release in the anaerobic reactor, the P removal increased from 4 to only 6 mgP/ℓ. The reason for this low increase in excess P removal is that the experimental units turned out to be poorly designed to achieve high P removals because the factors affecting the magnitude of excess P removal were not understood; once these factors were understood, it became possible to design processes capable of achieving high levels of excess P removal (see Figs 7.10 and 7.11).

the anaerobic reactor (S_{bsa}) surrounding the organisms is the key parameter determining whether or not P release and excess P uptake takes place.

To test the assumption above, it was necessary to develop a general equation by means of which S_{bsa} can be calculated:
Consider the anaerobic reactor in the UCT process,

$$S_{bsa} = (f_{bs}\ S_{bi} - \Delta S_{bs})/(1+r)\ (mgCOD/\ell) \qquad (7.1a)$$

and that in the Phoredox process

$$S_{bsa} = (f_{bs}\ S_{bi} - \Delta S_{bs})/(1+s)\ (mgCOD/\ell) \qquad (7.1b)$$

The term ΔS_{bs} is the concentration of readily biodegradable COD utilized for synthesis of cell material with nitrate (introduced via the r-recycle) and dissolved oxygen (introduced via the influent) serving as terminal electron acceptors. Because 8,6 mgCOD are utilized for the removal of 1 $mgNO_3$-N and 3,0 mgCOD with 1 mgO, (see Chapter 1), ΔS_{bs} can be expressed in terms of the nitrate in the r-recycle, N_{nr}, and the D.O. in the influent (O_i) and r-recycle (O_r), i.e.

for the UCT process

$$\Delta S_{bs} = r(8,6.N_{nr} + 3,0.O_r) + 3,0\ O_i \qquad (7.2a)$$

and for the Phoredox process

$$\Delta S_{bs} = s(8,6\ N_{ns} + 3,0.O_s) + 3,0\ O_i \qquad (7.2b)$$

where

N_n and O refer to the nitrate and D.O concentrations respectively. Symbols r and s and subscripts r,s and i refer respectively to the r- and s-recycles and the influent.

The calculation of S_{bsa} fortunately was possible because once the importance of the influent readily biodegradable COD fraction (f_{bs}) was recognized from the work on denitrification, it became standard experimental procedure to measure or determine almost daily, f_{bs}, f_{us}, f_{up}, S_{ti}, N_{nr}, O_r and O_i. Consequently Eqs (7.1) and (7.2) were

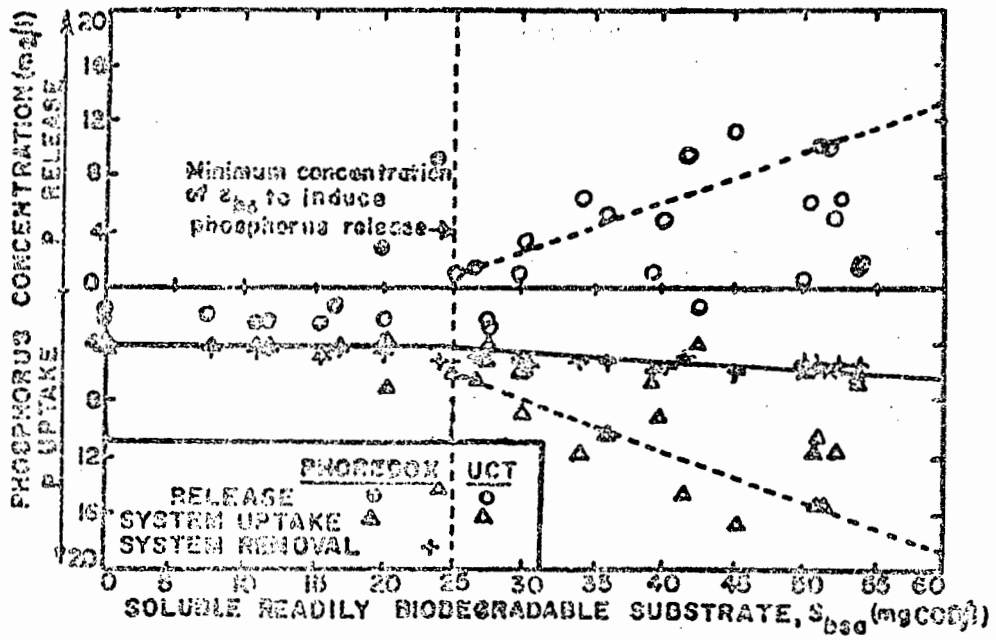

Fig 7.8 P release in the anaerobic reactor, process P uptake and process P removal versus readily biodegradable COD concentration in the anaerobic (S_{bsa}) for the modified Phoredox and UCT processes.

applied to the data used to plot Fig 7.7 and replotted in Fig 7.8 with S_{bsa} on the horizontal axis instead of the anaerobic capacity. From Fig 7.8 the following conclusions were drawn:

1) The minimum readily biodegradable COD concentration in the anaerobic reactor (S_{bsa}) to stimulate phosphorus release in the reactor is about 25 mgCOD/ℓ.

2) The degree of P release appears to increase as S_{bsa} increases above 25 mgCOD/ℓ, i.e. P release increases as (S_{bsa}-25) increases.

3) Excess phosphorus uptake is obtained only when phosphorus release takes place, and tends to increase with (S_{bsa}-25).*

The plots in Figs 7.7 and 7.8 show a striking similarity but on closer inspection, this similarity is more apparent than real. The similarity is there only for the UCT and Phoredox data: for these processes, the two sets of data fall in approximately the same position relative to

*See footnote on page 7.13.

the coordinate axes. This is so because in these processes, the principal contributor to A_c is the readily biodegradable COD in the influent, S_{bsi} - the contribution by the slowly biodegradable influent COD S_{bpi} is very small owing to the relatively small anaerobic sludge mass fractions (f_{xa}) - so that A_c and S_{bsa} are essentially equivalent parameters. In contrast, in the MLE process, the influent readily biodegradable COD S_{bsi} will have been completely utilized by the nitrate entering the anoxic reactor, i.e. $S_{bsa} = 0$. Nevertheless high A_c values are obtained from the S_{bpi} contribution because the unaerated sludge mass fractions are large. Consequently for the MLE process, there is no relationship between S_{bsa} and A_c. Hence in Fig 7.7, the MLE data fall in the right hand side of the plot (i.e. $A_c > 10$ mgNO_3-N/ℓ) whereas in Fig 7.8 they will fall in the left hand side of the plot (i.e. $S_{bsa} = 0$). Consequently, the MLE behaviour is incorrectly predicted by the A_c hypothesis (Fig 7.7) but correctly predicted by the S_{bsa} hypothesis (Fig 7.8). These results allowed the following statement to be made: A prerequisite for P release in the anaerobic reactor is that the concentration of readily biodegradable COD surrounding the organisms in the anaerobic reactor must exceed approximately 25 mgCOD/ℓ.

3.2 Magnitude of Excess Phosphorus Removal

A prerequisite for P release was stated above, however, the magnitudes of the P release and subsequent uptake and removal were not explicitly defined, once the prerequisite was satisfied. For this purpose an extensive and intensive investigation was inaugurated utilizing the UCT and modified UCT configurations. Series of tests were done under constant flow and load conditions: (1) at 14°C and 20°C, (2) using raw wastewater influents with COD's of 800, 500 and 300 mg/ℓ, and (3) varying the r-recycle and anaerobic mass fraction. In all the investigations the influent wastewater characteristics, i.e. COD, TKN, total P and readily biodegradable COD fraction f_{bs}, and filtered TKN, NH_4^+, NO_3^- and total P inthe process reactors were measured daily. In addition, all the normal parameters such as MLVSS, oxygen utilization rate, stirred settling velocity, pH and alkalinity were measured at regular intervals.

An analysis of these data* indicated that provided S_{bsa} > 25 mgCOD/ℓ,

1) for fixed r-recycle ratio and influent COD, increasing the volume of the anaerobic reactor (at the expense of the other reactor volumes) tended to increase P release and the P removal,

2) for fixed r-recycle ratio and anaerobic reactor volume, an increase in influent COD concentration tended to increase the P release and the P removal.

Although the trends stated above were evident it was not possible to identify a consistent behavioural pattern and it was concluded that the basic parameters had not been properly identified or isolated. In part, this was due to the interactive effects between the different parameters, for example, increasing the r-recycle ratio, (i) increases the mass of sludge passing through the anaerobic reactor, (ii) decreases the time the sludge is retained in the anaerobic reactor, (iii) increases the concentration of sludge in the reactor, and (iv) decreases the concentration of S_{bsa} in the anaerobic reactor (even if no nitrate is present in the r-recycle). With so many associated changes it was difficult to see directly which parameters are the significant ones. It was decided, therefore, to investigate the system theoretically on the basis of the perceived and hypothesized behaviour.

Considering Fig 7.8, the P release, uptake and removal appeared to be linearly related and it was decided to utilize the removal as the criterion against which to judge the effect of P any modification. As a consequence, P release *per se* was not incorporated into the hypothesis proposed to describe the P removal. The following behavioural pattern was hypothesized on the P removal based on experimental observations:

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*Detailed description of the experimental investigation is given in a report by Siebritz, Ekama and Marais (1983).

1) Excess P removal is obtained only when $S_{bsa} > 25$ mgCOD/ℓ.*

2) As S_{bsa} increases above 25 mgCOD/ℓ, so the P removal increases.

3) The longer the *actual* anaerobic retention (R_{an}), the higher the P removal.

4) The larger the mass of sludge recycled through the anaerobic reactor, the higher the P removal.

Scrutiny of (4) above showed that it could be transformed to a more useful equivalent,

4) The greater the mass of sludge recycled through the anaerobic reactor each day expressed as a fraction of the mass of sludge in the process, n, the higher the P removal.

The statements (2) and (4) above do not give an explicit quantitative expression of the expected behaviour. To obtain such an expression an hypothesis on the expected behavioural pattern of (2) to (4) has to be made. An hypothesis consistent with the observations is:

"When any one of the factors (S_{bsa}-25), R_{an}, or n, is zero, excess phosphorus removal will be zero."

From this hypothesis, the *simplest* form of an equation expressing the tendency of a process to achieve excess P removal is

$$P_f = (S_{bsa}-25).R_{an}.n \qquad (7.3)$$

where

P_f = excess phosphorus removal propensity factor.

If P_f as defined above describes the observed behaviour of the three parameters, then the P removal due to excess uptake in the sludge (P_s) should be a function of P_f, i.e.

$$P_s = f(P_f) \qquad (7.4)$$

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*S_{bsa} is the concentration after allowing for removal of S_{bsa} due to nitrate and oxygen entering the anaerobic reactor.

Now $R_{an}.n$ in equation (7.3) can be expressed in terms of the process configuration and operational parameters, and for both the UCT and Phoredox processes this term can be shown* to be equal to f_{xa} i.e. $R_{an}.n = f_{xa}$ where f_{xa} is the anaerobic sludge mass fraction. Substituting f_{xa} for $R_{an}.n$ in Eq (7.3) yields

$$P_f = (S_{bsa}-25)f_{xa}; \quad \text{when } S_{bsa} < 25, \ P_f = 0,0 \tag{7.5}$$

Hence for the UCT and Phoredox process, it was concluded that the propensity to give excess P removal under constant flow and load conditions is a function only of the magnitude of readily biodegradable COD concentration in the anaerobic reactor above 25 mgCOD/ℓ and the magnitude of the anaerobic sludge mass fraction.

3.3 Quantitative Model for Excess Phosphorus Removal

As excess P removal is accepted to be a biological activity, it can be assumed that, (i) only the active fraction of the sludge can take up phosphorus in excess, (ii) the phosphorus removal will increase as the proportion of phosphorus in the active mass increases, and (iii) the proportion of phosphorus in the inert fractions of the sludge will remain unchanged. Accepting these assumptions, Martin and Marais (1975) developed the following equation for phosphorus removal based on the steady state activated sludge process model presented by Marais and Ekama (1976) (see Chapter 4, Section 9) i.e.

$$P_s = S_{ti}\left\{\frac{(1-f_{us}-f_{up})Y_h}{(1+b_{hT}R_s)}(\gamma+f_p\, f\, b_{hT}R_s) + f_p\frac{f_{up}}{f_{cv}}\right\} \tag{7.6}$$

where

P_s = P removal from the wastewater by incorporation in the sludge (mgP/ℓ)

f_p = P content of the endogenous and inert fractions of the volatile mass (mgP/mgVASS)

γ = coefficient of excess P removal i.e. the P content of the active mass (mgP/mgVSSS)

*see Siebritz, Ekama and Marais (1982; 1983)

With the aid of Eqs (7.1, 7.2, 7.5 and 7.6), the coefficient of excess P removal γ and the P removal propensity factor P_f were calculated for daily sets of experimental data* measured over a period of 18 months. In calculating the daily γ and P_f data pairs, those data for which there were known causes that may have adversely or favourably influenced the process behaviour were discarded.** The remaining daily γ and P_f data pairs are shown plotted in Fig 7.9.

The data in Fig 7.9 shows considerable scatter although a definite trend is discernable. Some of the scatter can be attributed to the selection the data values in the calculation of P_f: The f_{bs}, nitrate and

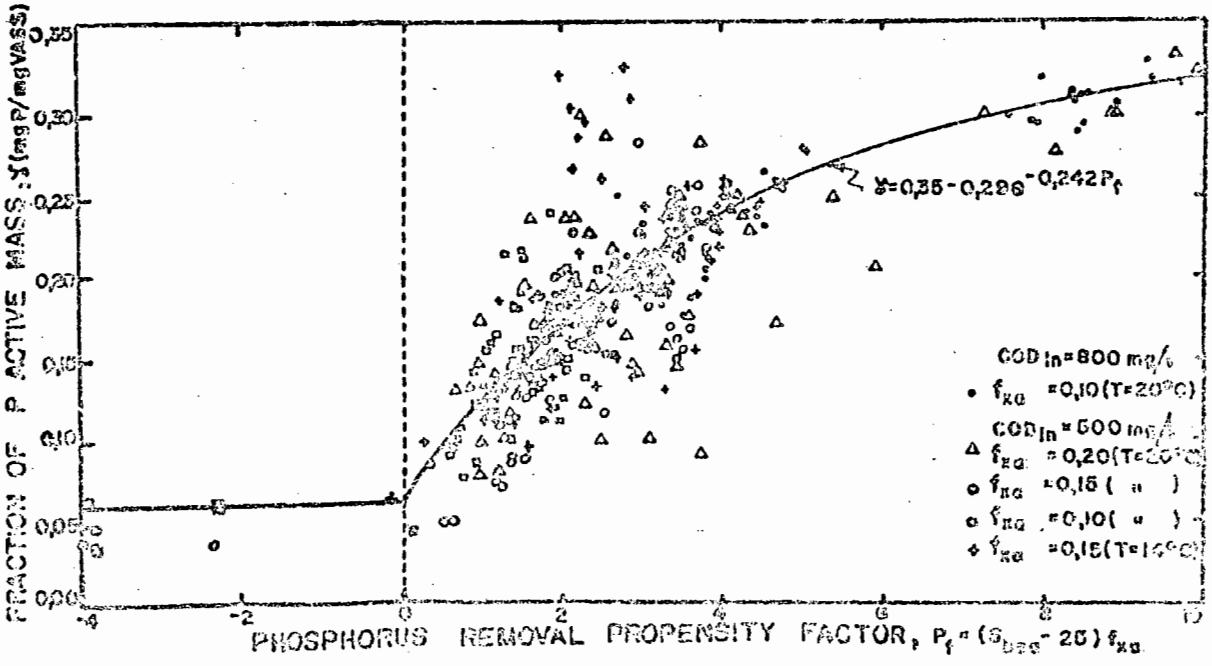

Fig 7.9 Coefficient of excess P removal (γ) versus P removal propensity factor (P_f) observed in the modified Phoredox, UCT and modified UCT processes at different anaerobic sludge mass fractions (f_{xa}), influent COD concentrations and temperatures.

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*The readily biodegradable COD fraction f_{bs} in the influent was measured in accordance with the procedure developed by Dold, Ekama and Marais (1980). Details of this procedure are given in Appendix 2.

**It was found that after a disruption of the process due to a mechanical breakdown, or a change in influent sewage characteristics or process parameter, the process required approximately 2 to 3 days to restabilize.

P removal values used in the calculations were all measured on the same day, i.e. the assumption was made that the response of γ to P_f is instantaneous. This, in fact, is not so; due to the long hold up time in the system it was repeatedly observed that the P removal response is out of phase with the input by some fraction of a day. (This is apparent in Fig 7.10 which records the observed and predicted P removal in one set of experiments).

Accepting the relatively large scatter, the form of the relationship and the constraints on the γ-P_f relationship were derived as follows: From Fig 7.9 apparently

i) there is an upper limit to γ, of about 0,35 at very high propensity factors,

ii) there is a lower limit to γ of about 0,06 at a propensity factor of zero,

iii) for propensity factors ranging from infinity to zero, the maximum change in γ is (0,35-0,06) = 0,29 and the decrease in γ with decrease in P_f appears to be of an exponential form.

On the basis of the above the following expression was chosen to represent the trend in the plotted data

$$\gamma = 0,35-0,29 \exp(-C.P_f)$$

The value of C was found by a least square analysis of the differences between the measured and predicted phosphorus removals and found to be equal to -0,242, i.e.

$$\gamma = 0,35-0,29.\exp(-0,242\ P_f) \quad (mgP/mgVASS) \qquad (7.7)$$

To check the predictive capacity of Eq (7.7), it was applied to the daily P_f data in all the five sets of experiments on the modified UCT, UCT and Phoredox processes in which S_{bsi} and the nitrate in the recycles were measured. (As stated above these sets of data covered influent COD values from 300 to 800 mg/ℓ at 14° and 20°C under a

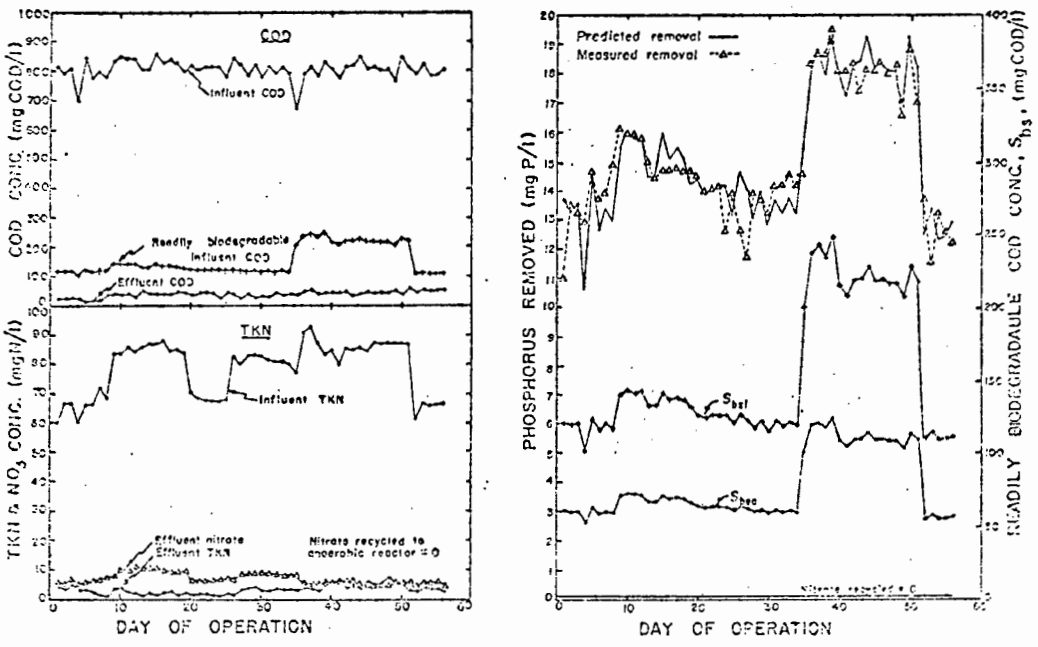

Fig 7.10 *Left*, daily experimental data of influent COD, TKN and readily biodegradable COD concentrations and nitrate concentrations in the effluent and the recycle to the anaerobic reactor and *Right* the measured and predicted phosphorus removal for a modified UCT process with the following sludge mass fractions; anaerobic 0,10, first anoxic 0,08, second anoxic 0,22, aerobic 0,60. (Data from Siebritz, Ekama and Marais, 1982b).

variety of TKN/COD ratios, anaerobic mass fractions from 0,10 to 0,20 and sludge ages 10* to 25 days. As an illustration two sets of data are shown in Figs 7.10 and 7.11 together with the predicted P removal values. Evidently the model gives a good prediction of the observed P removal. In Fig 7.10, the pronounced favourable effect of an increase in the readily biodegradable COD concentration (S_{bsi}) on the P removal, and in Fig 7.11 the depressing effect of nitrate in the recycle to the anaerobic reactor, are clearly illustrated.

The theory was tested further by feeding additional readily biodegradable COD (acetate and glucose) to the anaerobic reactor. Taking due account of the increased COD, again the predictions of P removal were in satisfactory correlation with those observed.

*The units in the short sludge age range were non nitrification-denitrification processes of the MLE configuration (Fig 7.4) with the first reactor anaerobic and the second aerobic.

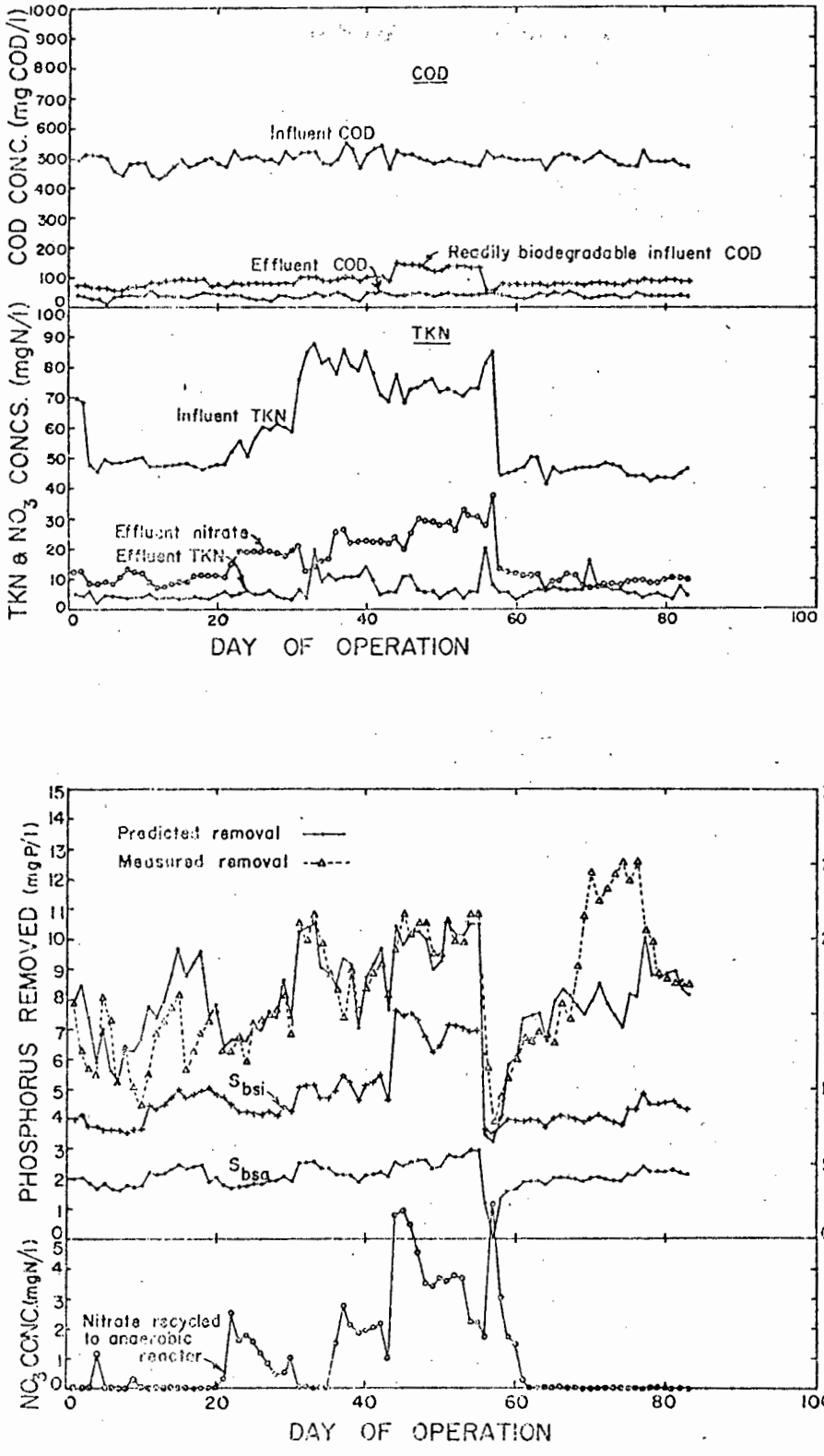

Fig 7.11 Response of a laboratory scale UCT process at 14°C, Anaerobic mass fraction = 0,15, Anoxic mass fraction 0,30. Aerobic mass fraction 0,55, Sludge age 20 days, treating unsettled flow from Mitchell's Plain. (Data from Siebritz, Ekama and Marais, 1983).

While doing a biodegradability investigation of the waste flow from the town of Caledon in South Africa, unexpected verification of the theory was obtained. The process configuration was a Modified Ludzack-Ettinger process (Fig 7.4) with an anoxic sludge mass fraction of 0,30 operated at 20 days sludge age, at 20°C, and with a mixed liquor (a) and an underflow (s) recycle ratio of 4:1 and 1:1 respectively. The wasteflow contained an industrial fraction (from a malting factory) constituting approximately 2/3 of the total COD load. The influent COD and TKN strengths were 1300 mg/ℓ and 70 mgN/ℓ respectively. It was found that the malting waste was virtually completely readily biodegradable resulting in a very high readily biodegradable COD fraction (f_{bs}) and concentration (S_{bsi}), 0,70 and 980 mgCOD/ℓ respectively. Taking due account of the diluting effect of the total recycle flow of 5 and the reduction of the readily biodegradable COD in the "anoxic" reactor by the nitrate discharged in the recycle flows (nitrification was complete, effluent TKN = 4 mgN/ℓ), the readily biodegradable COD concentration in the "anoxic" reactor (S_{bsa}) was estimated at 101 mgCOD/ℓ, the propensity factor (P_f) at 22,9 (Eq 7.5), the γ coefficient at 0,35 (Eq 7.7) to give an estimated P removal of 31 mgP/ℓ influent (Eq 7.6 with f_{us} = 0,05 and f_{up} = 0,06). The observed P removal was 29 mgP/ℓ. The results of this experiment should be contrasted with those discussed earlier on the Modified Ludzack-Ettinger processes. In those processes, no excess P removal was observed or predicted, even though the anoxic mass fraction was as high as 0,70, principally because the readily biodegradable COD concentration in the influent (S_{bsi}) was low and completely utilized in the anoxic reactor by the nitrate recycled to this reactor. Clearly if sufficient S_{bsi} is available and the TKN not excessive, it is possible to obtain high P removals even though the nitrate recycled to the anaerobic reactor is high, without having to resort to Phoredox or UCT configurations, provided the conditions for P release are satisfied as set out in Section 3.1 above.

At full scale Nicholls, Osborn and Marais (1982) and Nicholls (1982) tested the predictive power of the general nitrification-denitrification model on the Goudkoppies 5-stage Phoredox plant receiving an effluent that had passed through primary settling and then through an equalization

tank. The P removal behaviour of the plant was also monitored by measuring P conditions in the anaerobic and aerobic reactors and in the effluent. To evaluate both the model and P removal theory, *inter alia* the readily biodegradable COD in the influent discharged to the process (S_{bsi}) was measured, as described by Dold, Ekama and Marais (1980). The S_{bsi} was found to be very low due to its utilization by an anaerobic sludge layer that formed on the bottom of the unstirred equalization tank. In terms of the theory set out here the S_{bsi} was so low that with the 1:1 underflow recycle from the secondary settling tank to the anaerobic reactor, even if no nitrate was present in the recycle, S_{bsa} would be less than 25 mg/ℓ and consequently little excess P removal was to be expected, and, virtually no excess removal was observed for the plant. Measurements of S_{bsi} on the *influent* to the equalization tank however indicated that the S_{bsi} was sufficiently high that, if the equalization tank was bypassed, excess P removal was theoretically possible provided the nitrate in the underflow recycle to the anaerobic reactor could be maintained at less than 5 mgN/ℓ. Now at this point a computer-based equalization control strategy was implemented on the equalization tank (Dold, Buhr and Marais, 1982) and operated in such a fashion that any settled material was flushed daily from the tank. The flushing action prevented build-up of a sludge layer and effectively eliminated the loss of S_{bsi} in the tank. The process recycles in the plant were changed in accordance with those predicted by the general model to achieve maximum nitrate removal. As this removal was still insufficient to reduce the nitrate in the underflow recycle to less than 5 mgN/ℓ, the aerators next to the discharge points from the primary anoxic reactor were switched off, thereby effectively increasing the anoxic zone and further reducing the nitrate in the effluent. (Sufficient aerator capacity was available in the rest of the aeration basin not to affect the nitrification efficiency). In this fashion the nitrate was kept between 3 and 5 mgN/ℓ in the effluent and the underflow recycle. Under these conditions the predicted P removal was 4 to 5 mgP/ℓ influent; observed mean removal was 5 mgP/ℓ. The results from this investigation are particularly instructive because they demonstrate that little or no P removal is achievable if S_{bsi} is too low, or, where S_{bsi} is sufficiently high, although the potential

for removal is there, it will not be possible to realise this potential if nitrate in the recycle to the anaerobic reactor is so high that it reduces the S_{bsa} concentration to very low levels.

When investigating P removal behaviour in laboratory scale processes, batches of sewage usually were obtained from the outfall sewer and stored at 5°C for subsequent feed to the laboratory process units. Often it was noticed that with time the magnitudes of denitrification and P removal declined while feeding from the same raw sewage batch. Measurement of the readily biodegradable COD fraction of the daily feed taken from the cold storage batch indicated that normally there was a slow continuous loss of this fraction, giving rise to an associated reduction in denitrification and P removal. Hence, batches should not be stored longer than about one to one and a half weeks and the S_{bsi} in the feed should be measured daily. Furthermore, by monitoring the S_{bsi} on a routine basis, changes in S_{bsi} between batches are picked up that explain the "erratic" P removal behaviour noted earlier between different batches of sewage. Also, it is vitally important that the tanker transporting the batch to the laboratory, and the cold storage tank, are thoroughly cleaned between batches otherwise hydrogen sulfide generation and rapid loss of S_{bsi} will be encountered. High hydrogen sulfide concentration in the feed to a process can have adverse effects on the process response.

3.4 Comments on the Parametric Model and Recent Research Developments

The parametric model described above was developed from observed data on experimental processes operated under a wide range of conditions. The conditions ranged as follows:

(i)	Influent COD concentration	:	250 - 800 mgCOD/ℓ
(ii)	Readily biodegradable COD	:	70 - 220 mgCOD/ℓ
	i.e. fraction f_{ts}	:	0,12 - 0,27
(iii)	TKN/COD ratio	:	0,09 - 0,14
(iv)	Sludge age	:	13 and 25 days
(v)	Temperature	:	12°C and 20°C

Development of the model required the identification of the principal factors and conditions that appeared to influence the excess P removal and integration of these into a consistent quantitative expression for estimating the excess P removal. Summarizing, the main factors identified are

(i) As the concentration of readily biodegradable COD in the influent increased, so the excess P removal did likewise.

(ii) As the anaerobic sludge mass fraction increased so the excess P removal did likewise.

(iii) For identical conditions for (i) and (ii) above, as the sludge age *decreased*, so the excess P removal *increased*.

(iv) Temperature reduction appeared to have a slight positive effect on excess P removal.

The above tendencies formed the basis for structuring the formulations for estimating the excess P removal and the equations so derived were calibrated against the observed data (see Section 3.3 above). A comparison of the theoretically predicted and experimentally measured process P removal data for the conditions set out above is shown in Fig 7.12: clearly a good correlation is obtained.

> *It is of the greatest importance to note that the model is semi-empirical - its use must be limited strictly to within the ranges of process parameters and wastewater characteristics listed above. In particular, the model should not be used for design of plants with sludge ages less than about 14 days; in South Africa no research has been done on the process at short sludge ages and there is no certitude that the model predicts the behaviour adequately.*

Despite the good correlation, the parametric model is unsatisfactory from a scientific point of view because it is independent of any formal hypothesis on the biological mechanisms driving the process. Consequently the model should serve as an interim measure only for design and other practical purposes. What is required is a model based on fundamental biochemical and physical rules that will give rise to similar behavioural characteristics that formed the basis of the parametric model.

Historically important contributions towards developing such a model were made by Fuhs and Min Chen (1975) and the Johannesburg group (Nicholls, 1978). The latter group in particular, inaugurated a new approach which has influenced more recent hypothesized mechanisms

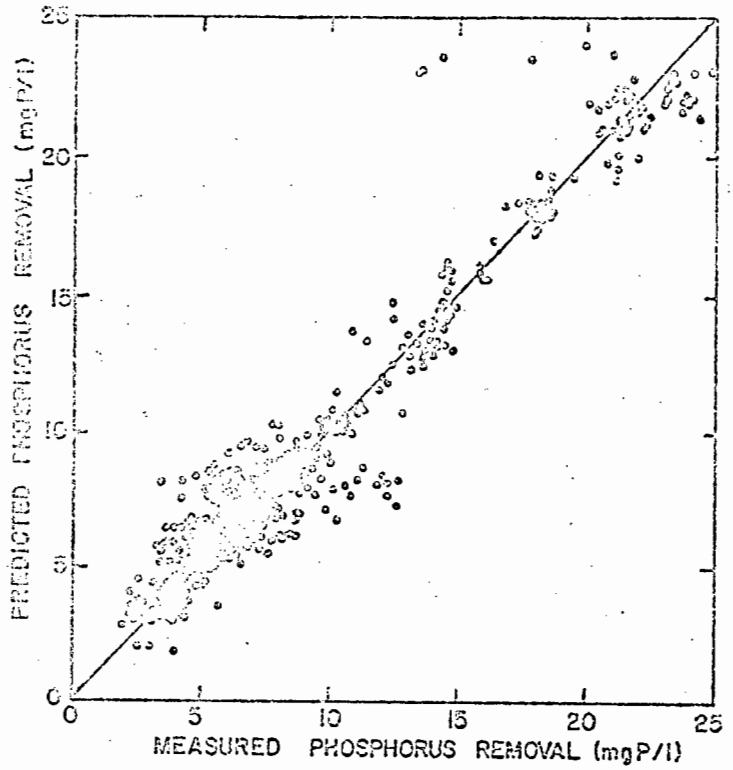

Fig 7.12 Comparison of measured P removals with those predicted by the parametric model for all the data observed under the different operating conditions.

proposed by Rensink (1981) and Marais *et al.* (1982). Preliminary indications are that a model based on the behaviour proposed by Rensink and Marais *et al.* has the potential to explain most of the behavioural characteristics of excess P removal and should in time allow a kinetic description to be incorporated into the general activated sludge process theory.

In essence, the basic concepts governing their model are as follows: Poly-P organisms, such as *Acinetobacter*, store phosphate internally as poly phosphate chains under aerobic conditions - some strains can do so also under anoxic conditions with nitrate serving as the electron acceptor. When poly-P organisms are discharged to an anaerobic reactor which receives the wastewater influent flow, the organisms survive the anaerobic conditions by breaking down some of the accumulated poly-P chains and the energy thereby released is utilized to complex the lower fatty acids surrounding the organisms

to higher forms, such as aceto-acetate or polyhydroxybutyrate and store these compounds internally. When the organisms thereafter enter an aerobic (or anoxic)* zone, they utilize the complexed compounds with oxygen (or nitrate)* as the electron acceptor for growth and replensihment of the poly-P stores.

If lower fatty acids were to be discharged to the *aerobic* (or *anoxic*) zones, the poly-P organisms would have to compete with the heterotrophs (or facultative heterotrophs) for this substrate because now it is available to these other organisms due to the presence of oxygen (or nitrate) as electron acceptor. However because the poly-P organisms are relatively slow growing compared to the other organisms, they will obtain only a minor fraction of the lower fatty acids in the aerobic reactor and consequently their growth will be very small. (This explains the reason why poly-P organisms are rarely found in considerable numbers in purely aerobic or anoxic-aerobic systems). Hence, by incorporating an anaerobic zone (which receives no nitrate from return recycle and to which the influent flow is discharged), the growth of the poly-P organisms is favoured, by allowing the organisms the opportunity to sequester the lower fatty acids by using their poly-P stores. In the anaerobic zone the other organisms are inoperative due to the unavailability of external electron acceptors.

With regard to the source of lower fatty acids for growth of the poly-P organisms this is present in the influent in the readily biodegradable COD fraction. However, not all the readily biodegradable COD is likely to be in a lower fatty acid form. Under these circumstances the behaviour of the facultative heterotrophs may well be advantageous to the poly-P organisms. In the anaerobic reactor the facultative organisms can derive a small amount of energy (principally for survival) by generating internal to itself an electron acceptor to break down the higher forms of readily biodegradable material (like glucose) to lower fatty acids, via the Embden-Meyerhof pathway.

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*Florentz and Granger (1982), using P^{31} nuclear magnetic resonance techniques, present evidence showing polyphosphate accumulation under anoxic conditions with nitrate serving as the electron acceptor.

Under anaerobic conditions these acids cannot enter the Krebs cycle because of the lack of an external electron acceptor, and the lower fatty acids formed by the facultative heterotrophs are released to the bulk liquid. In this way the poly-P organisms still can sequested lower fatty acids even though none might be available in the influent. In this fashion a slow growing organism like *Acinetobacter* can flourish in an anaerobic-anoxic-aerobic mixed culture system even though it may be an obligate aerobe. Apparently within the time scale of normal anaerobic zones, i.e. actual retention times up to 2 hours, a significant reduction of slowly biodegradable particulate COD to lower fatty acids is unlikely so that where lower fatty acid production does take place in the anaerobic reactor, this is principally from the readily biodegradable COD fraction.

In terms of the biochemical model the P released in the anaerobic zone is due to the utilization of poly-P reserves to provide energy for complexing the lower fatty acids. From stoichiometry (see Marais *et al.* 1982) for every P released there is an approximately constant mass of lower fatty acid complexed - the mass of poly-P organisms that will be formed depends on the mass of lower fatty acid complexed. The excess P removal attainable depends on the mass of poly-P organisms formed* which in turn depends on the proportion of mass of lower fatty acids and readily biodegradable COD in the influent that is complexed by the poly-P organisms.

Research of P release under batch anaerobic conditions using *acetate* as lower fatty acid (Law, Dold and Marais, 1982) has supported the above conclusions that there is an approximate proportionality between the mass of P released and the mass of acetate complexed - about 1 mgP/ℓ phosphate to 2 mgCOD/ℓ acetate. The rate of acetate complexing is very fast. Now in a normal municipal wastewater the lower fatty acid fraction of the readily biodegradable COD is likely to be low. Here the presence of the facultative heterotrophs may be important for the generation of the lower fatty acids. However, in this case the poly-P organisms can complex the lower fatty acids only

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* At steady state, the net number of poly-P organisms that form is equal to the number removed in the daily waste sludge. In essence excess biological P removal is the continuous formation of poly-P organisms and their removal from the process at a stage when they are filled with poly-P.

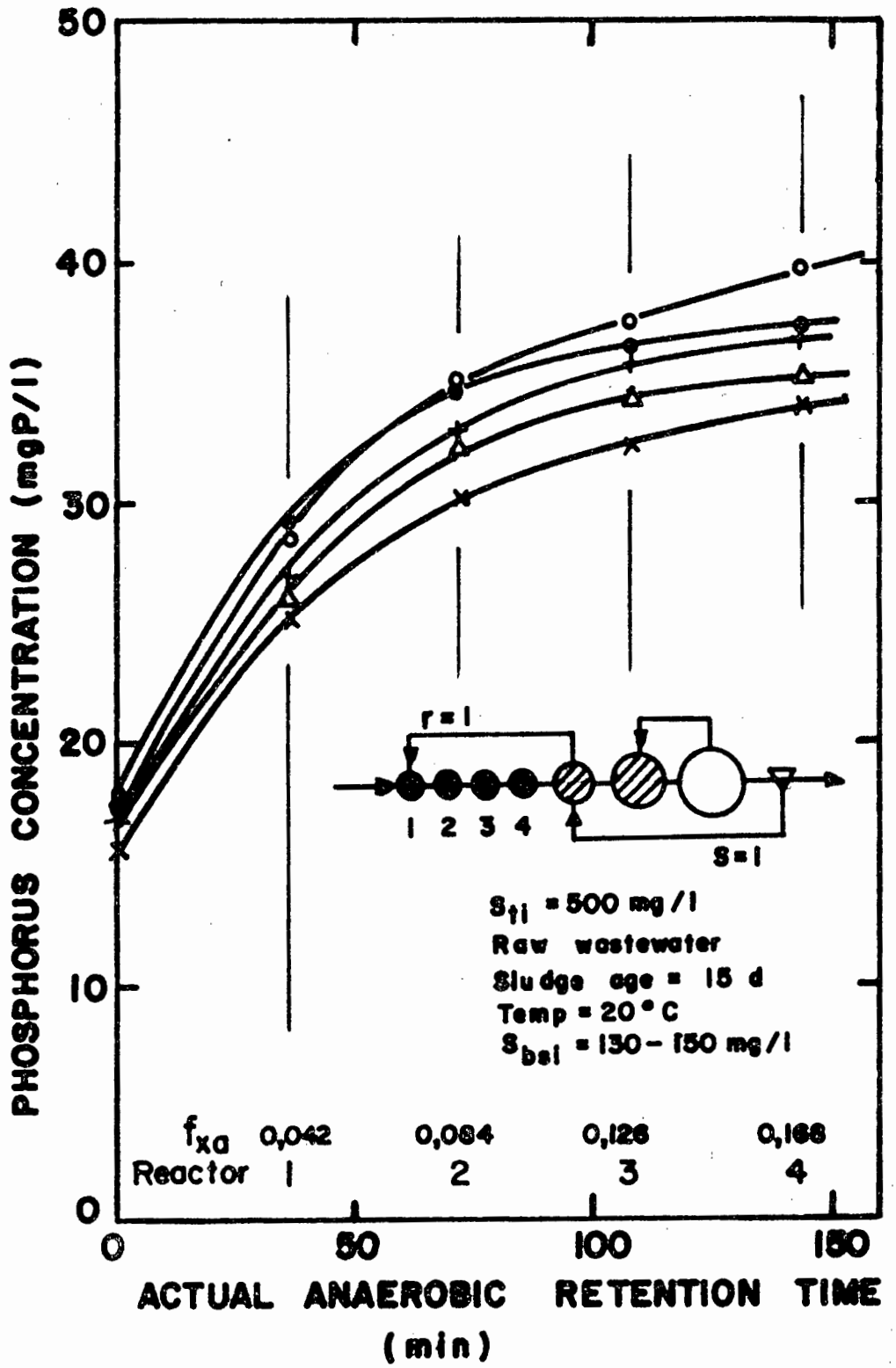

Fig 7.13a *Phosphorus concentration profile in a 4 in-series anaerobic reactor in a modified UCT process. S_{ti} = 500 mgCOD/ℓ raw wastewater, S_{bsi} ≅ 150 mgCOD/ℓ, sludge age 15 days, r-recycle ratio 1:1, temperature 20°C, MLVSS in anaerobic reactions 1450 mgVSS/ℓ.*

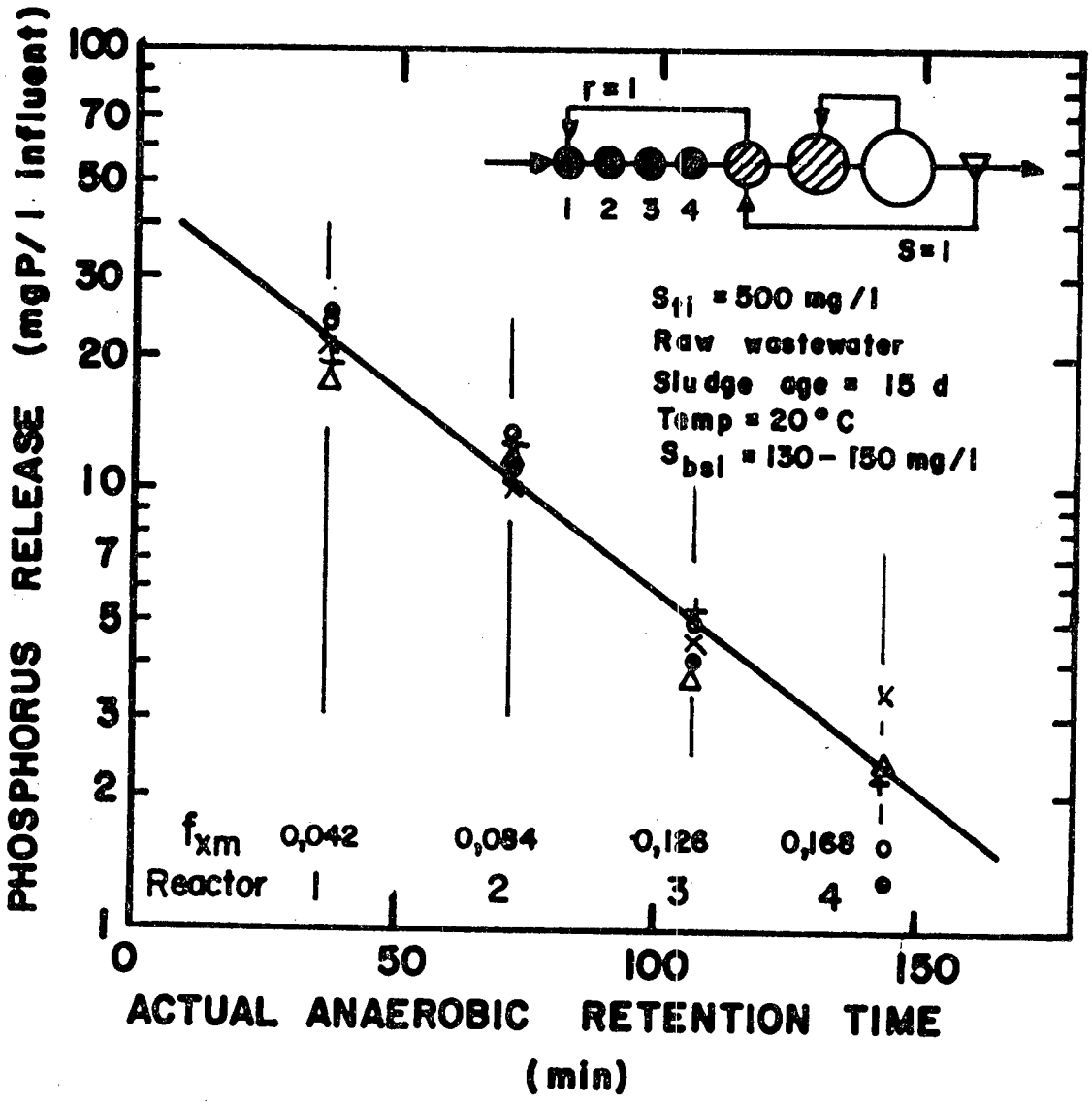

Fig 7.13b *Phosphorus release per reactor in 4 in-series anaerobic reactor. Data from Fig 7.13a.*

processes to be incorporated on the same plant (see Section 5 below).

Comparing the results of the experiments under batch conditions and under continuous conditions with plug flow and multi-compartment anaerobic reactors with those predicted by the parametric model, it appeared that there is an inconsistency. The results showed that P release is obtained for acetate and readily biodegradable COD concentrations below 25 mgCOD/ℓ whereas in the continuous experiments on which the parametric model is based this was apparently not so. The causes for the difference can be ascribed to (1) measurement procedure and (2) kinetic behaviour.

(i) Because the P concentration in the influent consists of two fractions i.e. a large soluble (80%) and a small particulate (~20%), an error is made when calculating the magnitude of the P release in the anaerobic reactor. In calculating the magnitude of the P release a mass balance on P across the anaerobic reactor is made and this is done by assuming that all the P entering and leaving the reactor is in a soluble form, even that of the influent. The limitation of this method of measuring the P release was realized and is probably the principal reason why in the parametric model it was found that the P content of the active mass (γ) once anaerobic conditions were imposed is 0,06 instead of the more usual value of 0,03 for purely aerobic processes i.e. P release probably did take place for $S_{bsa} < 25$ mgCOD/ℓ and this stimulated the additional P uptake from 0,03 to 0,06.

(ii) The parametric model indicates that apparently a minimum of 25 mgCOD/ℓ readily biodegradable COD in the anaerobic reactor is needed to induce excess P removal. A reason for this behaviour now can be advanced in terms of the kinetics describing the rate of P release observed on the series anaerobic reactors. A model has been constructed incorporating the kinetic P release hypothesis and all the data observed to date processed. The model predicts P uptake that is not as good as that obtained by the parametric model; evidently it requires further development. In consequence the model will

not be described here. However on one aspect of the model predictions deserve mention. Evidently for sludge ages of 20 days and anaerobic mass fraction of 0,15 influent COD of raw sewage 500 mg/ℓ and S_{bsi} = 100 mg/ℓ (the "normal" conditions tested in the experimental investigation) in the anaerobic reactor only about 70 - 80 percent of the readily biodegradable COD is sequestered i.e. ± 20 to 30 mg/ℓ COD is discharged from the anaerobic reactor - this would explain why (S_{bs}-25) appears in the parametric model. If however the anaerobic reactor is subdivided into 2 or more reactors the S_{bs} in the effluent from such a series reduces to 5 to 10 mg/ℓ. The effluent S_{bs} furthermore depends on the influent S_{bs} so that it would seem the factor (S_{bs}-25) is only an approximation.

The discrepancies discussed above are not crucial to the predictive power of the parametric model - a series of calculations using the kinetic and parametric approaches show that significant differences arise only for low strength COD wastewaters, and here the parametric model tends to predict lower removals than the kinetic model. However, the kinetic model is not yet verified or developed sufficiently to replace the parametric model.

The above discussion is not intended to cast doubt on the parametric model and its usefulness; that can clearly be seen in Figs 7.10, 7.11 and 7.12. The parametric model evolved out of an intensive research programme to develop an understanding of and design criteria for biological nutrient removal processes with little emphasis on kinetics. In the future, it is very likely that it will be superseded by a more elegant kinetic model without necessarily leading to very much better predictions. However, for the present, the parametric model is probably the best and most exhaustively tested model available and can be of great value for analysing biological P removal process behaviour as it is understood at present. The remaining part of this Chapter will demonstrate the use of the parametric model for design.

4. IMPLICATIONS OF THE MODEL ON DESIGN

The parametric model for excess biological P removal consists essentially of two concepts i.e. (i) the coefficient of excess P removal (γ) and (ii) the excess P removal propensity factor (P_f), which are linked by an empirical relationship, Eq (7.7).

4.1 Coefficient of Excess P removal (γ)

When excess P removal takes place, this will be reflected in the magnitude of the coefficient of excess P removal γ in Eq (7.6), the value being greater than 0,02 to 0,03 mgP/mgVASS usually found for purely aerobic processes. With excess P uptake found in processes incorporating anaerobic reactors, can range from a minimum of about 0,06 to a maximum of about 0,35 when the appropriate anaerobic conditions are present.

A plot of Eq (7.6) (divided through by S_{ti}) versus sludge age (R_s) is given in Fig 7.14 for raw and settled wastewater (see Tables 4.3, 5.2 and 6.1) at 14°C and 22°C assuming a constant γ value of 0,18 mgP/mgVASS, a value readily attained in appropriately designed P removal plants. Figure 7.14 shows that the mass of P removed per mgCOD in the influent,

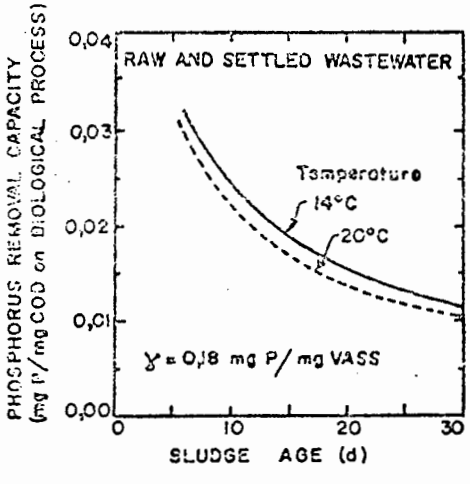

Fig 7.14 Phosphorus removal per kg COD load on biological process versus sludge age for an excess P removal coefficient (γ) of 0,18 mgP/mgVASS at 14°C and 20°C for raw and settled wastewaters.

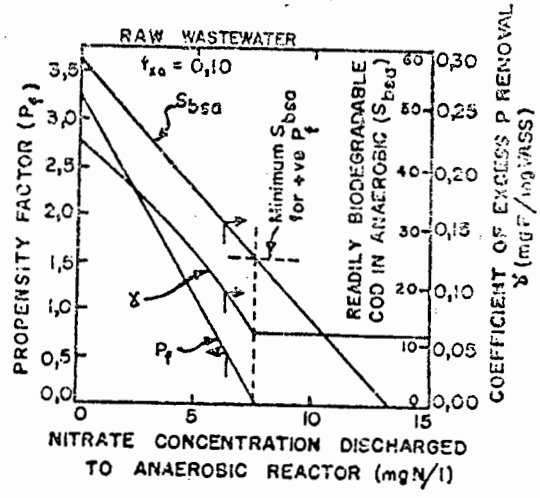

Fig 7.15 Propensity factor (P_f), rapidly biodegradable COD concentration in anaerobic reactor (S_{bsa}) and coefficient of excess P removal (γ) versus the nitrate concentration discharged to the anaerobic reactor for an anaerobic sludge mass fraction (f_{xa}) of 0,10 for raw wastewater.

P_s/S_{ti}, decreases sharply with sludge age so that *to remove the maximum P, the sludge age should be kept as low as possible.* The P removal per unit COD load is approximately the same for raw and settled sewage. Hence, because primary sedimentation removes as much as 40% of the COD load, P removal with settled wastewater is about 40% less than with raw wastewater. For a constant γ the effect of temperature on removal is small because the nett mass of sludge produced does not change significantly with temperature.

4.2 Excess P Removal Propensity Factor (P_f)

The magnitude of the coefficient of excess P removal γ is influenced by a number of conditions in the anaerobic reactor: (1) the magnitude of the readily biodegradable COD (S_{bsa}) in excess of 25 mgCOD/ℓ, (ii) the actual retention time and (iii) the mass of sludge (expressed as a fraction of the mass of sludge in the process) passing through the anaerobic reactor each day. These conditions were quantified for the UCT and Phoredox processes and formalized into the parameter called the excess P removal propensity factor (P_f) given by Eq (7.5). The readily biodegradable COD concentration in the anaerobic reactor (S_{bsa}) for the UCT and Phoredox processes can be calculated from Eqs (8.1 and 7.2). These predictions are based on the model derived from observations on processes with sludge ages between 15 and 25 days. Where the sludge ages are outside the limits, in particular where the sludge ages are less than 15 days, it would be unwise to extrapolate the model to these conditions.

4.3 Excess P Removal Model

The coefficient of excess P removal (γ) and the propensity factor (P_f) described above were linked with an empirical relationship i.e. Eq (7.7) found from data given in Fig 7.9. Equation (7.7) shows that the higher the P_f factor, the greater the γ coefficient. Consequently, at a fixed sludge age, the higher the P_f factor in a process, the greater the P removal per unit COD load (P_s/S_{ti}). For a fixed f_{xa}, high P_f factors are obtained with (i) high influent COD concentrations (for normal f_{bs} fractions in the wastewater of about 20%) (ii) high readily biodegradable COD fractions (f_{bs}) and (iii) a zero nitrate concentration in the recycles to the anaerobic reactor (N_{nr} and N_{ns} = 0). The sensitivity of excess P removal to nitrate discharged to the anaerobic reactor is demonstrated in Fig 7.15. In Fig 7.15, the S_{bsa} concentration, P_f factor and γ coefficient calculated from Eqs (7.1, 7.2, 7,5 to 7.7) for the raw wastewater characteristics given in Tables 4.3, 5.2 and 6.1 are plotted versus the nitrate concentration discharged to the anaerobic reactor for an anaerobic sludge mass fraction f_{xa} = 0,10, underflow recycle ratio s = 1, D.O. in s-recycle O_s = 1,0 mgO/ℓ and D.O. in influent D_i = 0,0 mgO/ℓ. It can be seen that for nitrate concentrations > 7 mg/ℓ, the γ coefficient is reduced to one third of the value for a zero nitrate concentration; at 25 days sludge age and 14°C, this reduction in γ from 0,22 to 0,07 mgP/mgVASS, results in a decline in P removal from 9,3 to 3,5 mgP/ℓ. This example demonstrates that for good P removal, nitrate discharge to the anaerobic reactor should be avoided.

5. DESIGN PROCEDURE*

When selecting a Phoredox or UCT process for excess P removal, it is necessary to establish whether or not near complete denitrification can be achieved for the selected sludge age (R_s) and maximum specific growth rate of the nitrifiers at 20°C (μ_{nm20}). If near complete denitrification can be achieved for sludge ages less than about 25 days and total anoxic sludge mass fractions (f_{xdt}) less than about 0,40 at

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*The design procedure described in this section has been published in a shorter form by Ekama, Siebritz and Marais (1982).

the minimum temperature (T_{min}), then a Phoredox process is indicated; if it cannot be achieved, then a UCT process is indicated.

For the P removal processes, an anaerobic reactor is required for the stimulation of excess P removal, so that the maximum *anoxic* sludge mass fraction available for denitrification (f_{xdm}), is the difference between the maximum unaerated sludge mass fraction (f_{xm}) and the selected anaerobic sludge mass fraction (f_{xa}) i.e.

$$f_{xdm} = f_{xm} - f_{xa} \qquad (7.8)$$

where f_{xm} is given by Eq (5.32) for a selected R_s, μ_{nm20}, S_f and T_{min}.

The denitrification behaviour of the Phoredox process is identical to that of the Bardenpho process, i.e. Eqs (6.25 to 6.29) apply. Note however, that f_{xdm} for the Phoredox process is given by Eq (7.8) whereas f_{xdm} for the Bardenpho process is given by Eq (6.24). Hence for the same unaerated sludge mass fraction f_{xm}, the Phoredox process has a lower f_{xdm} than the Bardenpho process, by an amount equal to f_{xa}. Now from the behaviour of the Bardenpho process (see Chapter 6,Section 7), it was shown that when the wastewater characteristics are favourable, in particular, a high readily biodegradable COD fraction (f_{bs}), a high μ_{nm20} value and a low TKN/COD ratio, near complete denitrification can be achieved at sludge ages around 20 to 25 days (see Fig 6.17). Consequently for favourable wastewater characteristics near complete denitrification, and hence excess P removal can be achieved in the Phoredox process (because the effluent nitrate concentration is low and hence little nitrate is discharged to the anaerobic reactor). The excess P removal attainable, P_s, is calculated with the aid of the parametric model described above and knowing P_s, the effluent P concentration P_{te} given by the difference between the influent P concentration P_{ti} and P_s i.e.

$$P_{te} = P_{ti} - P_s \text{ (mg P/}\ell\text{)} \qquad (7.9)$$

In the design of a Phoredox process for a selected sludge age, if it is found that the total anoxic sludge mass fraction for complete

denitrification f_{xdt} is less than the maximum allowed f_{xdm}, the following options are open:

1) f_{x1} and f_{x3} can be increased to give a total anoxic sludge mass fraction equal to f_{xdm} which introduces a factor of safety for denitrification, the magnitude of which is equal to f_{xdm}/f_{xdt}.

2) The sludge age can be reduced so that f_{xdm} becomes equal to f_{xdt}. The lower sludge age will allow a saving in process volume (see Fig 4.3). This lower sludge age R_s, can be estimated as follows: set f_{xdm} equal to f_{xdt} required for complete denitrification at T_{min}; determine f_{xm} from Eq (7.8); with f_{xm} calculate R_s from Eq (5.32); to check repeat step by step procedure for the new R_s.

3) For the Phoredox process, f_{xa} can be increased to improve excess P removal, so that $f_{xdm} = f_{xdt}$ from Eq (7.8).

Options (2) and (3) above are not recommended as these exclude a factor of safety in denitrification: Exclusion of a factor of safety on denitrification for the Phoredox process may have serious consequences because the discharge of *any* nitrate to the anaerobic reactor reduces the P removal attainable in the process (Fig 7.15).

For design purposes where the Phoredox process is to operate between temperatures T_{min} and T_{max}, the following sequence of calculations needs to be made to check whether or not complete denitrification can be achieved in a Phoredox process and, if so, to select the optimal process configuration for N and P removal:

Step 1 : Select wastewater characteristics; S_{ti}, N_{ti}, P_{ti}, f_{bs}, f_{up}, f_{us}, μ_{nm20}, T_{max}, T_{min}.

Step 2 : Select R_s and S_f.

Step 3 : Calculate f_{xm} for T_{min} from Eq (5.32).

Step 5 : Estimate N_{te} for T_{max} and T_{min}.

Step 6 : With f_{up} and f_{us}, calculate N_s for T_{max} and T_{min} for selected R_s from Eq (4.23).

Step 7 : Calculate N_c from Eq (5.33)

Step 8 : Select f_{xa}.

Step 9 : Calculate D_{pp} from Eq (6.25) for T_{max} and for T_{min} with f_{xdm} given by Eq (7.8).

Step 10 : Select s, O_a and O_s.

Step 11 : Calculate f_{x1min} from Eq (6.21) for T_{max} and for T_{min}.

Step 12 : Calculate f_{x3min} from Eq (6.29) for T_{max} and for T_{min}.

Step 13 : Select the a-recycle ratio and calculate N_{ne} for T_{min} from Eq (6.

Step 14 : If $N_{ne} < 0$, set $N_{ne} = 0$.

Step 15 : With N_{ne} calculate f_{x1}, f_{x3} and f_{xdt} from Eqs (6.26 to 6.28).

Step 16 : Check that $f_{x1} \geq f_{x1min}$ and $f_{x3} \geq f_{x3min}$. If not, discard selected a-recycle ratio as invalid.

Step 17 : Repeat steps 12 to 15 for different a-recycle ratios.

Step 18 : Repeat steps 12 to 16 for T_{max}.

Step 19 : Fix f_{x1} and f_{x3} by procedure given in Chapter 6, Section 6.2. This fixes N_{ne} and hence N_{ns}.

Step 20 : Select O_i.

Step 21 : Calculate ΔS_{bsa} from Eq (7.2b).

Step 22 : Calculate S_{bsa} from Eq (7.1b).

Step 23 : Calculate P_f from Eq (7.5).

Step 24 : Calculate γ from Eq (7.7)

Step 25 : Calculate P_s from Eq (7.6).

Step 26 : Calculate P_{te} from Eq (7.9).

Step 27 : Is P_{te} sufficiently low? If not, decrease R_s or increase f_{xa} at expense of f_{xdm}; however improvement will only be achieved if $f_{xdt} < f_{xdm}$ i.e. $N_{ne} < 0{,}0$; if $f_{xdt} = f_{xdm}$ i.e. $N_{ne} > 0$, changes will increase P_{te}.

Step 28 : Repeat calculations for T_{max}.

Step 29 : Can required P_{te} be achieved with the Phoredox process? if not, select a UCT process.

When the required P removal cannot be attained in the Phoredox process due to incomplete denitrification, the UCT or Modified UCT processes are the indicated processes.* The configuration of the UCT processes is such that the conditions in the anaerobic reactor are independent of the denitrification behaviour for TKN/COD ratios up to about 0,13. Hence in their design, the P removal can be estimated from the conditions in the anaerobic reactor without the need to know the extent of denitrification i.e. N and P removal can be dealt with separately in the design of these processes.

In the design for excess P removal in the UCT process, the readily biodegradable COD concentration in the anaerobic reactor (S_{bsa}) can be found directly from Eq (7.1a and 7.2a) without the need for selecting R_s or μ_{nm20}: S_{bsa} depends only on the influent COD strength (S_{ti}), the readily biodegradable COD fraction (f_{bs}) and the r-recycle ratio from the anoxic to the anaerobic reactor. The r-recycle ratio usually is

*It is possible to design a Modified Phoredox/Modified UCT/UCT process combination, see later in this section.

selected at 1:1; higher ratios lead to greater dilution of S_{bsa} with a concomitant reduction in P removal and lower values lead to inordinately large anaerobic reactor *volume* fractions with respect to the anaerobic sludge *mass* fractions (see Eqs 7.10 to 7.11). Selecting r = 1 and the nitrate (N_{nr}) and D.O (O_r) concentrations in the r-recycle of say 1 mgN/ℓ and 1 mgO/ℓ to include a factor of safety for excess P removal, then S_{bsa} can be calculated from Eqs (7.1a and 7.2a) and will remain unchanged irrespective of the temperature. Knowing S_{bsa}, the propensity factor P_f can be calculated from Eq (7.5) for a selected anaerobic sludge mass fraction f_{xa}, and from the P_f value, the γ coefficient can be calculated from Eq (7.7). Knowing γ, the P removal from the particular wastewater can be calculated from Eq (7.6) for a selected sludge age (R_s). The P removal should be determined at T_{max} because, for a constant S_{bsa} or γ, the P removal at T_{max} is less than at T_{min} (Fig 7.6). Hence, for various values of f_{xa}, the P removal at different sludge ages can be calculated, and estimates of f_{xa} and R_s giving the desired or optimal P removal can be found. In selecting f_{xa}, it is recommended that f_{xa} should not be less than 0,10 and not greater than 0,20: for $f_{xa} < 0{,}10$, the P removal usually will be inadequate even at relatively short sludge ages for normal wastewaters, particularly for settled wastewaters; for $f_{xa} > 0{,}20$ no UCT experimental response data are available so that the parametric model has not been calibrated to include the process behaviour for $f_{xa} > 0{,}20$.* At $f_{xa} = 0{,}20$, the process has been found to operate satisfactorily (Siebritz *et al.* 1982b). With regard to selecting R_s, cognizance must be taken of its effect on the maximum unaerated sludge mass fraction f_{xm} (Eq 5.32) because, with f_{xa} fixed, f_{xm} fixes the maximum anoxic sludge mass fraction f_{xdm} (Eq 7.8) which, in turn, governs the degree of denitrification that can be achieved.

Once f_{xa} and R_s are selected, the denitrifiction can be calculated by applying the design equations for N removal in the MLE process, except that f_{xdm} is given by the difference between f_{xm} and f_{xa} (see Eq 7.8).

For design purposes, where the process is to operate between temperatures T_{min} and T_{max}, the following sequence of calculations is recommended to facilitate selection of the optimal process configuration

*Laboratory and pilot scale data on process behaviour for $f_{xa} > 0{,}20$ is available from the NIWR (see Interim Design Guide by NIWR).

for N and P removal in the UCT process:

Step 1 : Select wastewater characteristics; S_{ti}, N_{ti}, P_{ti}, f_{bs}, f_{up}, μ_{nm20}, T_{max}, T_{min}.

Step 2 : Select r (usually 1,0) and N_{nr} and O_r (say 1 mg/ℓ each).

Step 3 : Calculate S_{bsa} from Eqs (7.1a and 7.2a).

Step 4 : Select f_{xa} (between 0,10 and 0,20).

Step 5 : Calculate P_f from Eq (7.5) and γ from Eq (7.7).

Step 6 : Select R_s.

Step 7 : Calculate P_s from Eq (7.6) for T_{max} and for T_{min}.

Step 8 : Calculate P_{te} from Eq (7.9) for T_{max} and for T_{min}.

Step 9 : Is P_{te} adequate? If not repeat steps 4 to 8 for increased f_{xa} and/or R_s (see Design Chart Fig 7.15).

Step 10 : Select S_f.

Step 11 : Calculate f_{xm} for T_{min} from Eq (5.32).

Step 12 : With f_{xm} and R_s calculate S_f for T_{max} from Eq (5.32).

Step 13 : Estimate N_{te} for T_{max} and T_{min}.

Step 14 : With f_{up} and f_{us}, calculate N_s for T_{max} and T_{min} for selected R_s from Eq (4.23).

Step 15 : Calculate N_c from Eq (5.33)

Step 16 : Calculate D_{pp} from Eq (6.25) for T_{max} and for T_{min} with f_{xdm} given by Eq (7.8).

Step 17 : Select s, O_a and O_s.

Step 18 : Calculate a_o from Eq (6.30) and N_{ne} from Eq (6.31).

Step 19 : Are P_{te} and N_{ne} adequate? If P_{te} is too high, increase f_{xa} or reduce R_s - these changes will increase N_{ne}; If P_{te} is too low, decrease f_{xa} or increase R_s - these changes will decrease N_{ne}.

Step 20 : Repeat from steps 4 to 17 until required or optimal P_{te} and N_{ne} is obtained.

Having completed the design for the UCT process, if the influent TKN/COD ratio is less than about 0,11 to 0,12 mgN/mgCOD, the process may be converted to a modified UCT process (Fig 7.6). The conversion is done by subdividing the *anoxic* sludge mass fraction (f_{xdm}) into two sub-fractions; the first is usually allocated a sludge mass fraction f_{xd1} of about 0,10, and the second, f_{xd2}, having the remaining sludge mass fraction i.e. $f_{xd2} = f_{xdm} - f_{xd1}$. Having made this subdivision, the possibility of operating the modified UCT process (Fig 7.6) as a UCT process (Fig 7.5) is not excluded; by making provision that the r-recycle flow to the anaerobic reactor can be taken from either the first or the second anoxic reactors, the process can be operated as either a modified UCT or a UCT process (Fig 7.16). The advantages of operating the process as a modified UCT process were set out in Section 2.2.3 above (see also Chapter 3, Section 4).

It is necessary to check whether or not the modified UCT/UCT process combination can be operated as a modified UCT process. For successful operation of the modified process, the denitrification potential of the first anoxic reactor must be greater than, or at least equal to the equivalent nitrate load on the reactor at the *minimum expected temperature* (T_{min}). The denitrification potential is calculated by substituting $f_{xd1} = 0,10$ for f_{x1} in Eq (6.20). The equivalent nitrate load is found from the effluent nitrate concentration (N_{ne}) from the UCT process, the s-recycle ratio and the D.O. concentration in the s-recycle (O_s)

i.e. the equivalent nitrate load is $s(N_{ne} + O_s/2,86)$. For TKN/COD ratios < 0,12 mgN/mgCOD, it will be found that the denitrification potential is sufficient to denitrify the equivalent nitrate load with a reasonable factor of safety (S_{fd}) of say 1,3. Where S_{fd} is the rate of the denitrification potential and the equivalent nitrate load on the first anoxic reactor.

By setting $f_{xd1} = 0,10$, usually it will be found that the reactor is sufficiently large for complete utilization of the influent readily biodegradable COD (S_{bsi}). This can be checked by means of Eq (6.21). If T_{min} is less than 14°C, it may be found from Eq (6.21) that 0,10 is insufficient for complete utilization of the S_{bsi}. In this event, f_{xd1} can be increased slightly to a maximum of 0,12. Values of $f_{xd1} > 0,12$ are not recommended because for temperatures $> T_{min}$, the reactor will be over-designed leading to a reduced nitrogen removal efficiency of the process. By designing the first anoxic reactor (f_{xd1}) to allow the possibility of complete or near complete utilization of the S_{bsi}, the process can achieve excess P removal up to the TKN/COD ratio at which S_{bsi} is completely utilized. This TKN/COD ratio can be calculated by trial and error by testing increasing TKN/COD ratios on the process.

Generally it will be found that the higher the TKN/COD ratio, the lower the factor of safety S_{fd} for complete denitrification of the equivalent nitrate load on the first anoxic reactor. When $S_{fd} < 1,1$, the prospect of operating the modified UCT/UCT process combination as a modified UCT process has little merit. This limit is strongly dependent on the influent readily biodegradable COD fraction f_{bs}: For normal f_{bs} ratios in raw wastewaters of 0,20 to 0,25, it will be found that S_{fd} is less than 1,1 for TKN/COD ratios above 0,11 to 0,12 mgN/mgCOD at a minimum temperature of 14°C. When the f_{bs} fraction and TKN/COD ratio of the influent are such that operation of the

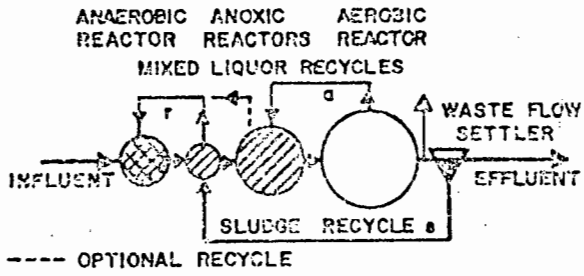

Fig 7.16 The modified UCT/UCT process combination for biological P and N removal.

modified UCT process is not possible then it must be operated as a UCT process. In the UCT process, if the a-recycle ratio is too low to produce an actual anoxic retention time lower than 1,5 hours, poor sludge settling characteristics may be obtained, and should be taken into account in the design of the secondary settling tanks (see Chapter 12).

When the influent readily biodegradable COD fraction and TKN/COD ratio are such that operation of a modified UCT process is possible, the mixed liquor a-recycle ratio is set at the greater value of two lower limits i.e. (1) that which loads the second anoxic reactor to its denitrification potential or (2) that which will produce an actual anoxic retention time of less than 1 hour. The first limit is calculated with the aid of Eq (6.30) except that D_{pp} is replaced by the denitrification potential of the *second* anoxic reactor, which can be calculated by substituting the anoxic sludge mass fraction of the second anoxic reactor f_{xd2} for f_{x1} in Eq (6.20). The second limit is found by calculating the volume of the second anoxic reactor as set out below (see Section 7.5 above) and with the specified s-recycle ratio and influent flow rate, finding the a-recycle ratio which would produce an actual retention time of 1 hour.

A problem with the design of a nutrient removal process is that at the design stage the wastewater characteristics, in particular the TKN/COD ratio and maximum specific growth rate of the nitrifiers at 20°C (μ_{nm20}), are not sufficiently accurately known to design an optimal nutrient removal process. With regard to the μ_{nm20} value little can be done (besides measuring it, van Haandel (1981) and Sehayek (1981) with Marais) other than selecting a conservative value. However, with regard to the TKN/COD ratio virtually complete process flexibility can be provided for, so that depending on the TKN/COD ratio, the process can be operated as a Modified Phoredox, Modified UCT and UCT process. A schematic diagram of a process with this flexibility is given in Fig 7.17 (incorporation of the 5 stage Phoredox is difficult due to the problem of having to convert the secondary anoxic reactor to an aerobic reactor). Note in Fig 7.17 that the anaerobic sludge mass fraction is subdivided into 4 equal sized compartments in series. The reason for this is twofold;

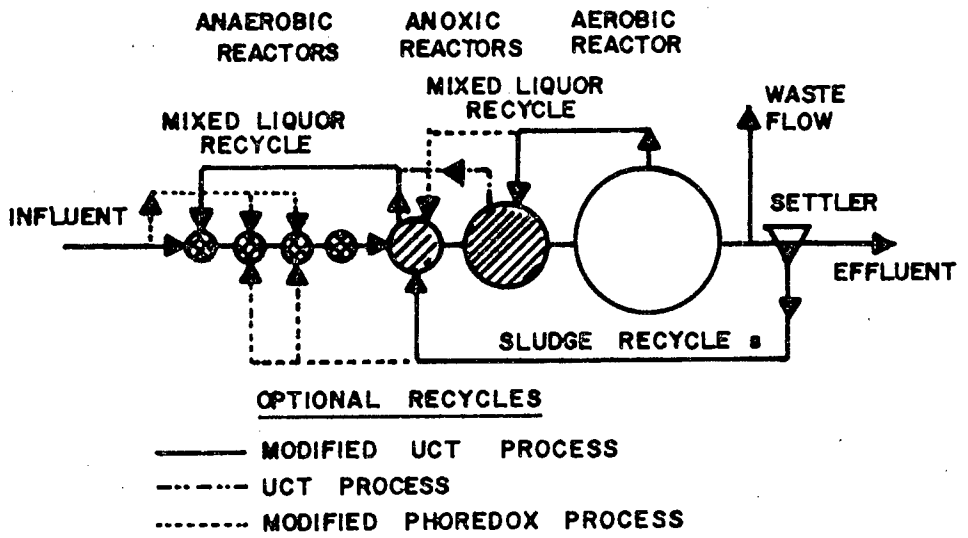

Fig 7.17. Schematic process configuration layout showing additional and optimal recycles and flows allowing operation as a Modified Phoredox, Modified UCT or UCT process.

(1) From a practical point of view, for the same anaerobic reactor volume, the UCT process has an anaerobic sludge mass fraction half that for the Modified Phoredox process. Consequently in the design, the anaerobic volume must be such that when the process is operated as a UCT process, the required anaerobic sludge mass fraction is retained. If then the process is required to be operated as a Modified Phoredox, the first and second compartments can be bypassed thereby allowing the same anaerobic sludge mass fraction to be used for the Modified Phoredox process. It should be noted that if the anaerobic volume is not reduced when converting to a Modified Phoredox, the *aerobic* sludge mass fraction will be reduced, and this reduction may be detrimental for achieving nitrification, particularly at the lower temperatures. The equations for calculating the relationship between the volume fractions and sludge mass fractions for the different processes are given in Section 7.5 below.

(2) From a theoretical point of view, the kinetics of biological excess P removal are such that for the same total anaerobic sludge mass fraction subdivision into a number of equal sized completely mixed compartments in series is more efficient than a single completely mixed reactor (see Section 3.4 above). Theoretically the greater the number of compartments in series the better but practically very little advantage is gained with more than 3. In the proposed composite configuration (Fig 7.17), the anaerobic zone comprises of 4 compartments when operated as a UCT process and 2 when operated as a Modified Phoredox. With the Modified Phoredox consideration could be given to utilizing three of the four anaerobic compartments but caution should be exercised in not increasing the anaerobic sludge mass fraction too much because its increase is at the expense of the *aerobic* sludge mass fraction with the result that nitrification and/or phosphorus uptake may be adversely affected (see Chapter 10).

The design calculations for the Phoredox and UCT processes set out above will be demonstrated with the aid of worked examples after the presentation of a design chart for graphically estimating the excess P removal attainable.

6. DESIGN CHART

The excess biological P removal theory described in Section 3 above can be summarized in a design chart (see Fig 7.18). For a raw or settled wastewater, the chart is constructed as follows:

(i) In the bottom right hand quadrant, a graph of total influent COD concentration (S_{ti}) versus readily biodegradable COD concentration (S_{bsi}) for various readily biodegradable COD fractions (f_{bs} or f_{ts}) is plotted from Eqs (2.8a or 2.9a).

(ii) In the top right hand quadrant the propensity factor P_f versus

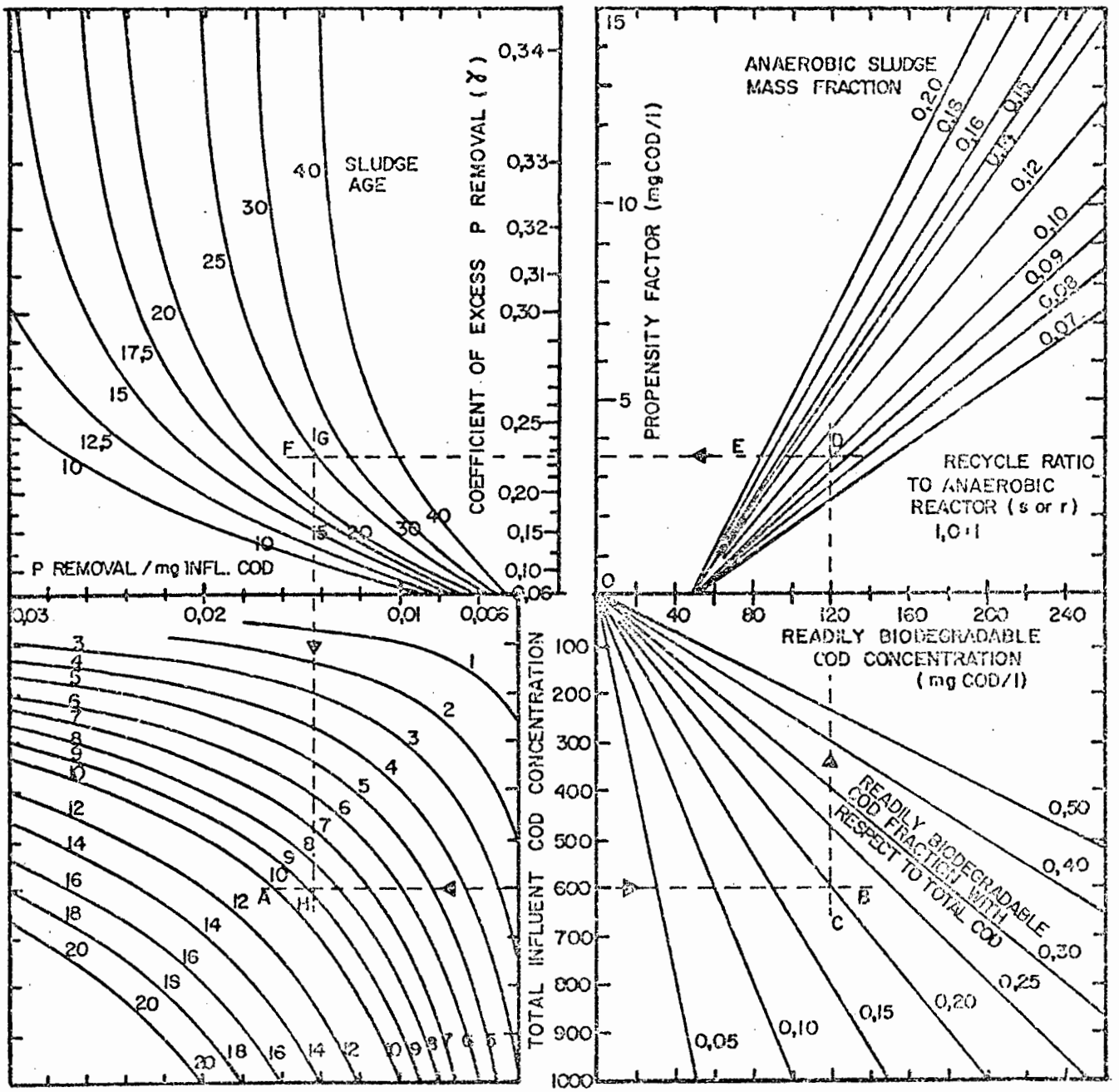

Fig 7.18 Design chart for graphically estimating the excess P removal attainable in nutrient removal processes at 14°C treating raw wastewater provided no nitrate is discharged to the anaerobic reactor.

S_{bsi} is plotted for different anaerobic sludge mass fraction (f_{xa}) and fixed recycle ratio to the anaerobic (r or s) assuming say no nitrate or dissolved oxygen is discharged to the anaerobic reactor from Eqs (7.1 or 7.2 and 7.5).

(iii) The left hand side of the P_f axis is rescaled in terms of γ by means of Eq (7.7).

(iv) In the upper left hand quadrant a graph of P removal per unit COD (P_s/S_{ti}) versus γ is plotted for different sludge ages for fixed temperature from Eq (7.6).

(v) In the bottom left hand quadrant, a graph of P_s versus S_{ti} is plotted for fixed removals of P in mg/ℓ.

The diagram constructed by the above procedure is valid for the selected wastewater characteristics f_{up} f_{us} and Temperature. An example of such a diagram is given in Fig 7.18 for the typical raw wastewater characteristics given in Table 4.3. In the construction of the diagram, it is assumed that no nitrate (and dissolved oxygen) is discharged to the anaerobic reactor. Consequently the chart is valid for (i) the Phoredox process provided that complete denitrification can be achieved so that the nitrate concentration in the under flow recycle is zero, (ii) the UCT process provided the mixed liquor a-recycle ratio is carefully controlled so that it does not overload the primary anoxic reactor with nitrate and (iii) the modified UCT process provided the effluent nitrate concentration is sufficiently low so that the underflow recycle does not overload the first anoxic reactor with nitrate.

The design chart is used as follows: For the raw wastewater characteristics given in Table 4.3 (i.e. f_{up} = 0,13, f_{us} = 0,05) and taking a temperature of 20°C, draw a horizontal line at the influent COD concentration S_{ti} of 600 mg COD/ℓ (line AB). Now the readily biodegradable COD fraction with respect to total COD (f_{ts}) is 0,20 (i.e. f_{bs} = 0,24, the fraction with respect to the biodegradable COD).

Moving to the right; where line AB cuts the f_{ts} = 0,20 line, draw a vertical line (line CD). Moving upwards along line CD; where line CD cuts the selected anaerobic sludge mass fraction line (say 0,10), draw a horizontal line (line EF). Moving left along line EF; the intercepts with the P_f and γ axes give the values of these parameters. Where line EF cuts the selected sludge age line (say 25 days), draw a vertical line (line GH). Moving downwards along line GH; the intercept with the P_s/S_{ti} axis gives the value of this parameter, and moving further down, the P removal in mgP/ℓ is given at the intercept of lines GH and AB i.e. 8,8 mgP/ℓ. Hence the P removal for a raw wastewater with S_{ti} = 600, f_{ts} = 0,20 (f_{bs} = 0,24), f_{xa} = 0,10 and R_s = 25 days at T = 20°C is 8,8 mgP/ℓ. Clearly, with the aid of the diagram, the effect of changing R_s, f_{xa} and f_{ts} (f_{bs}) on P removal can readily be ascertained (subject to the provisos mentioned above for the different processes).

7. DESIGN EXAMPLES

The design of excess P removal in nutrient removal processes by means of the procedure set out above is demonstrated by continuing the numerical example given in Chapter 4, Section 12 (in which the design procedure for organic material removal was demonstrated), Chapter 5, Section 8 (in which the behaviour of nitrification was demonstrated) and Chapter 6, Section 7 (in which nitrogen removal was demonstrated). The wastewater characteristics used in the design example, which are those of a typical raw and settled municipal wastewater, have all been defined and are given in Tables 4.3, 5.2 and 6.1. The causes and effects of variability in some of these characteristics, such as temperature, denitrification rates, readily biodegradable COD fraction etc. have been discussed in detail in Chapter 6, Sections 7.1 and 7.2.

Many of the decisions related to the design of excess P removal in a nutrient removal process are contingent upon the nitrogen removal behaviour of the process. Consequently, in the design example continuous reference to the design examples for nitrogen removal will be made, i.e. Chapter 6, Section 7 and a thorough understanding of this section, and nitrogen removal in general, will be presumed.

7.1 The Phoredox Process

In the calculations for nitrogen removal in the Bardenpho process treating the *raw wastewater* at 25 days sludge age and 14°C, it was found th a total anoxic sludge mass fraction (f_{xdt}) of 0,40 was required to achieve complete denitrification (see Table 6.3). Now the total unaerated sludge mass fraction (f_{xm}) was found to be 0,50. Hence the largest anaerobic sludge mass fraction (f_{xa}) to effect excess P removal in a Phoredox process, (which requires near complete denitrification to achieve good excess P removal)(see Chapter 3, Section 4) is 0,50-0,40 = 0,10 (from Eq 7.8). Because complete denitrification can be achieved with f_{xdt} = 0,40, the nitrate concentration in the underflow recycle (N_{ns}) is zero, and, taking the D.O. concentration in the underflow recycle (O_s) as 1 mgO/ℓ, the readily biodegradable COD in the anaerobic reactor (S_{bsa}) for an underflow recycle ratio (s) of 1 is found from Eqs (7.1b and 7.2b) i.e.

$$\Delta S_{bs} = 1(8,6.0 + 3,0.1) + 0$$

$$= 3$$

$$S_{bsa} = \{0,24(1- \ 0,13-0,05) \ 600 - 3\}/(1 + 1)$$

$$= 57,5 \text{ mgCOD}/\ell.$$

The propensity factor P_f is found from Eq (7.5) i.e.

$$P_f = (57,5-25).0,10 = 3,25 \text{ mgCOD}/\ell$$

and the coefficient of excess P removal γ is found from Eq (7.7) i.e.

$$\gamma = 0,35 - 0,29\exp(-0,242.3,25)$$

$$= 0,218 \text{ mgP/mgVASS}.$$

Hence the P removal at 25 days sludge age and 14°C is found from Eq (7.6) i.e.

$$P_s = 600 \{ \frac{(1-0,05-0,13)0,45}{(1+0,20.25)} (0,218 + 0,015.0,20.0,20.25) + 0,015.0,13/1,48 \}$$

$$= 600 \{ 0,0615 (0,218 + 0,015) + 0,0013 \}$$

$$= 600.0,0156$$

$$= 9,4 \text{ mgP}/\ell.$$

The influent P concentration is 10 mgP/ℓ so that with 9,4 mgP/ℓ removal, the effluent P concentration P_{te} is 10,0-9,4 = 0,6 mgP/ℓ (see Eq 7.9). Similarly, the P removal at 22°C is found to be 8,0 mgP/ℓ. Note that S_{bsa}, P_f and γ remain unchanged at different temperatures but P_s is decreased because b_h in Eq (7.6) is increased to 0,25/d at 22°C (see Table 4.1). The important design results are listed in Table 7.1.

In the design of the Phoredox process above, f_{xa} was set at the maximum value leaving a just sufficiently large f_{xdt} to attain complete denitrification. This leaves the Phoredox process in a critical state because to achieve the estimated P removals, complete denitrification should be achieved (see Fig 7.15). However, this cannot be guaranteed because there is no factor of safety on the denitrification. To introduce a factor of safety on the denitrification two options are open; (i) the primary anoxic sludge mass fraction (f_{xl}) can be increased, but this will have to be at the expense of a reduction in f_{xa} (because f_{xm} is fixed at 0,50 to achieve nitrification) but a reduction in f_{xa} will cause a reduction in P removal - from the design chart at 20°C (Fig 7.18) a reduction in f_{xa} from 0,10 to 0,07 reduces the P removal from 8,8 to 7,7 mgP/ℓ, (ii) the sludge age can be increased allowing a larger unaerated sludge mass fraction (f_{xm}), and hence, with f_{xa} fixed at 0,10, allowing a larger anoxic sludge mass fraction (f_{xdm}). However, the sludge age not only requires a larger process volume, but also reduces the P removal - from the design chart

Table 7.1 Summary of design calculations for the Phoredox and UCT processes treating raw or settled wastewater at 25 days sludge age (Wastewater characteristics given in Tables 4.3, 5.2 and 6.1).

Parameter	Symbol	Units	Raw Wastewater				Settled Wastewater			
			Phoredox		UCT		Phoredox		UCT	
Temperature	T	°C	14	22	14	22	14	22	14	2
Safety factor	S_f		1,25	2,7	1,25	2,7	1,25	2,7	1,25	2
Max.unaerated sludge mass	f_{xm}		0,50	0,50	0,50	0,50	0,50	0,50	0,50	0
Effluent TKN	N_{te}	mgN/ℓ	3,0	2,0	3,0	2,0	3,0	2,0	3,0	2,
N for sludge production	N_s	mgN/ℓ	12,6	12,0	12,6	12,0	5,7	5,4	5,7	5
Nitrification capacity	N_c	mgN/ℓ	32,4	34,0	32,4	34,0	32,3	33,6	32,3	3
Anaerobic sludge mass	f_{xa}		0,10	0,10	0,10	0,10	0,10	0,10	0,10	0,
Max.anoxic sludge mass	f_{dxm}		0,40	0,40	0,40	0,40	0,40	0,40	0,40	0,
Max.denit.potential	D_{pp}	mgN/ℓ	37,2	49,7	37,2	49,7	27,2	35,4	27,2	3
D.O. in a-recycle	O_a	mgO/ℓ	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,
D.O. in s-recycle	O_s) O_r)	mgO/ℓ	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,
Underflow recycle ratio	s		1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,
Prim.anoxic sludge mass	f_{x1}		0,16	0,16	0,40	0,40	0,26	0,26	0,40	0,
Sec.anoxic sludge mass	f_{x3}		0,24	0,24	-	-	0,14	0,14	-	-
Total anoxic sludge mass	f_{xdt}		0,40	0,40	0,40	0,40	0,40	0,40	0,40	0,
Optimum a-recycle ratio	a_o		3,3	4,2	5,0*	5,0*	1,3	3,0	2,5	5,
Effluent nitrate	N_{ne}	mgN/ℓ	0,0	0,0	4,6	4,8	8,0	4,8	7,2	4,
Nitrate recycled to anaerobic reactor	N_{ns} } N_{nr} }	mgN/ℓ	0,0	0,0	0,0	0,0	8,0	4,8	0,0	0,
Readily bio.COD in anaerobic reactor	S_{bsa}	mgCOD/ℓ	57	57	57	57	16,5	30,0	50,8	5C
Propensity factor	P_f	mgCOD/ℓ	3,3	3,3	3,3	3,3	0,00	0,50	2,57	2,
γ coefficient		mgP/ℓ mgVASS	0,22	0,22	0,22	0,22	0,06	0,093	0,195	0,
P removal	P_s	mgP/ℓ	9,4	8,0	9,4	8,0	1,9	2,3	5,1	4,
Effluent P concentration	P_{te}	mgP/ℓ	0,6	2,0	0,6	2,0	6,6	6,2	3,4	4,

* These are not the calculated optimum values but are values at the practical and economical limit (see Chapter 6, Section 7.5).

(Fig 7.18), an increase in R_s from 25 to 30 days (which increases f_{xdt} from 0,40 to 0,43) reduces the P removal from 8,8 mgP/ℓ to 7,6 mgP/ℓ. Clearly the raw wastewater influent TKN/COD ratio (i.e. 0,08) is just on the limit for successful implementation of the Phoredox process - any increase in TKN/COD ratio will result in significant concentrations of nitrate in the effluent and underflow recycle (> 3 mgN/ℓ) which, when discharged to the anaerobic reactor, will cause a deterioration in P removal (Fig 7.15).

From the above, it is clear that the TKN/COD ratio of the settled wastewater (i.e. 0,114) is too high to attain excess P removal in the Phoredox process. This is demonstrated in the calculations below: For this process operating at 25* days sludge age with f_{xa} = 0,10* and hence f_{xdm} = 0,40, from the denitrification theory an N_{ne} of 4,8 mgN/ℓ is obtained at 22°C with f_{x1} = 0,26, f_{x3} = 0,14, a_o = 3,0 and N_{ne} = 8,0 mgN/ℓ at 14°C with a_o = 1,3 (see Table 7.1). At 14°C, with 8 mgN/ℓ nitrate in the effluent and underflow s-recycle, and taking the s-recycle ratio to be specified at 1:1, and contains a D.O. concentration (O_s) of 1 mgO/ℓ, then from Eqs (7.1b and 7.2b), the readily biodegradable COD concentration in the anaerobic reactor (S_{bsa}) is only 16,5 mgCOD/ℓ, which is too low for stimulating excess P removal. Hence from Eq (7.5) the propensity factor (P_f) is 0,0 and from Eq (7.7), the γ coefficient is at its minimum of 0,06 mgP/mgVASS. From Eq (7.6), with γ = 0,06, the P removal (P_s) at R_s = 25 and T = 14°C is 1,9 mgP/ℓ, which, from Eq (7.9), with P_{ti} = 8,5 mgP/ℓ gives an effluent P concentration (P_{te}) of 6,6 mgP/ℓ, (see Table 7.1). A similarly poor P removal is obtained also at 22°C (see Table 7.1). Clearly when the wastewater characteristics are such that near complete denitrification cannot be obtained, the Phoredox process will not function as an efficient biological P removal facility.

7.2 The UCT Processes

In the UCT processes, the complicating effect of the possibility of a discharge of nitrate to the anaerobic reactor is absent. Consequently, in such a design, the nitrogen and phosphorus removal aspects can be

*Selected the same as for the raw wastewater case so that a direct comparison can be made between the settled and raw wastewaters.

dealt with separately and the P removal in the processes can be calculated without first having to determine the effluent nitrate concentration.

In the design of the UCT or modified UCT processes, first the UCT process (Fig 7.5) is designed and once this is complete, a check is made as to whether or not this configuration can be converted to a modified process (Fig 7.6). It is recommended that where it is possible to convert the UCT process to a modified one, the option of operating the modified process as a UCT process should always be included (see Fig 7.16). Consider also the option of incorporating the Modified Phoredox/Modified UCT/UCT combination (see Fig 7.17).

At the same sludge age, anaerobic sludge mass fraction and temperature, the P removal attainable in the UCT process is the same as that attainable in the Phoredox process with complete denitrification i.e. when no nitrate is discharged to the anaerobic reactors of both processes. Consequently, with the UCT process operating at 25* days sludge age with f_{xa} = 0,10*, the P removal from the *raw wastewater* is 9,4 mgP/ℓ at 14°C and 8,0 mgP/ℓ at 22°C. Note also that for the same process parameters R_s, f_{xa}, f_{xdm} and temperature, the nitrification capacity N_c and denitrification potential D_{pp} for the UCT process are identical to those for the Phoredox process. The nitrogen removal behaviour of the UCT process is identical to that of the MLE process and hence the effluent nitrate concentration N_{ne} and optimum mixed liquor a-recycle ratio a_o are found from N_c and D_{pp} with the aid of Eqs (6.30 and 6.31); from Eq (6.30), a_o at both 14°C and 22°C is greater than the practical limit of 5 and hence a_o is limited at 5 which gives N_{ne} at 14°C and 22°C as 4,6 mgN/ℓ and 4,8 mgN/ℓ respectively from Eq (6.31). The important design details emerging from the above calculations are given in Table 7.1. A comparison of the Phoredox and UCT process will be given once the design of the UCT process treating the settled wastewater has been demonstrated.

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*Selected the same so that a direct comparison between the Phoredox and UCT process can be made. A design with different R_s and f_{xa} to effect better P removal (at the cost of poorer N removal) will be presented below.

With the UCT process treating the *settled wastewater* at 25 days sludge age and an anaerobic sludge mass fraction of 0,10, the P removal is calculated from the theory (note that now, the P removal is not the same as that in the Phoredox process because with the settled wastewater in this process, nitrate is discharged to the anaerobic reactor). Taking the nitrate recycled to the anaerobic reactor in the UCT process as 0,0 and an r-recycle ratio of 1:1 with a D.O.concentration (O_r) of zero mgO/ℓ, the readily biodegradable COD concentration in the anaerobic reactor (S_{bsa}) is found from Eqs (7.1a and 7.2a) i.e.

$$\Delta S_{bs} = 1\ (8,6.0 + 3,0.1) + 3,0.0$$

$$= 3 \text{ mg COD}/\ell$$

$$S_{bsa} = \{\ 0,33.(1-0,08-0,04).360-3\}/(1+1)$$

$$= 50,8 \text{ mgCOD}/\ell.$$

The propensity factor P_f is found from Eq (7.5) i.e.

$$P_f = (50,8-25).0,10 = 2,58 \text{ mgCOD}/\ell$$

and the γ coefficient is found from Eq (7.7) i.e.

$$\gamma = 0,35-0,29\exp\ (-0,242.2,58)$$

$$= 0,195 \text{ mgP/mgVASS}$$

Hence the P removal P_s at 25 days sludge age and 14°C is found from Eq (7.6) i.e.

$$P_s = 360\ \{\frac{(1-0,08-0,04)0,45}{(1+0,20.25)}\ (0,195 + 0,015.0,20.0,20.25) + 0,015.0,04/1,48\}$$

$$= 5,1 \text{ mgP}/\ell.$$

The effluent P concentration P_{te} is given by Eq (7.9) i.e.

P_{te} = 8,5-5,1 = 3,4 mgP/ℓ.

Similarly, P_s and P_{te} at 22°C are 4,3 and 4,2 respectively.

The nitrogen removal behaviour of the UCT process is found from Eqs (6.30 and 6.31) - note that the nitrification capacity N_c and denitrification potential D_{pp}, with f_{xdm} = 0,40 are identical to those of the Phoredox process. At 14°C the effluent nitrate concentration N_{ne} and optimum a-recycle ratio a_o are 7,2 mgN/ℓ and 2,5 and at 22°C, the calculated a_o is greater than the practical limit of 5 and with a = 5, N_{ne} = 4,8 mgN/ℓ. Important design details of the N and P removal design are given in Table 7.1.

7.3 Comparison of Phoredox and UCT Processes

Comparing the Phoredox and UCT processes at 25 days sludge age and anaerobic sludge mass fraction of 0,10 (see Table 7.1), it can be seen that for the *raw wastewater*, the Phoredox and UCT processes achieve the same excess P removals, but the N removal is better in the Phoredox than in the UCT process; the former achieves complete denitrification whereas the latter produces an effluent nitrate concentration of 5mgN/ℓ. However, the Phoredox process is in a critical state in that an unexpected increase in TKN/COD ratio above 0,08 will result in a deterioration in excess P removal. In contrast the UCT process can accommodate unexpected increases in TKN/COD ratio up to about 0,13 (0,11 for the modified process), while maintaining its calculated excess P removal of 9,4 mgP/ℓ at 14°C; this flexibility is at the cost of producing a minimum effluent nitrate concentration of 5mgN/ℓ.

From the above results, the following general conclusion can be made: For wastewaters with TKN/COD ratios and readily biodegradable COD fractions such that the Phoredox process can achieve good excess P removals, its effluent nitrate concentration will be near zero. For the same conditions the UCT process will also achieve good excess P removal but its effluent nitrate concentration will be 5 to 6mgN/ℓ.

In the Phoredox process, the good effluent quality is at the cost of process flexibility to accommodate unexpected TKN/COD ratio increases; this flexibility is incorporated in the UCT process but it is at the cost of a poorer effluent quality. In these situations (which usually arise with wastewater of TKN/COD ratio less than 0,08 with 20 to 25% readily biodegradable COD fraction, f_{ts}), the process to select would depend on the variability in TKN/COD ratio of the wastewater.

Comparing the Phoredox and UCT processes treating the *settled wastewater* with a TKN/COD ratio of 0,114, it can be seen that both processes produce approximately similar effluent nitrate concentrations (see Table 7.1). However, with respect to excess P removal, the Phoredox process can be seen to have a poorer P removal facility than the UCT process; the difference arises from the fact that in the Phoredox process, the exclusion of nitrate from the anaerobic reactor becomes impossible once near complete denitrification cannot be achieved, whereas in the UCT process, this is possible up to TKN/COD ratios of about 0,13 (depending on the f_{bs} (f_{ts}) fraction).

7.4 Redesign of the UCT Process

Although in the UCT process the exclusion of nitrate from the anaerobic reactor is possible, thereby allowing the greatest potential for P removal, the actual P removal attained in the process for the settled wastewater is insufficient to reduce the effluent P concentration (P_{te}) below 1 mgP/ℓ. This is because the anaerobic sludge mass fraction (f_{xa}) and sludge age (R_s) have been incorrectly selected to attain $P_{te} < 1$ mgP/ℓ. To improve the P removal, R_s needs to be reduced and f_{xa} increased. From the design chart for raw wastewater (Fig 7.18), if f_{xa} is increased from 0,10 to 0,15 and the sludge age decreased from 25 to 20 days, the estimated P removal (at 20°C with no nitrate and D.O. recycled to the anaerobic reactor) is 11,5 mgP/ℓ.

Accepting an anaerobic sludge mass fraction of 0,15 and the sludge age of 20 days, the design of the UCT process for raw and settled wastewater at 14°C and 22°C was undertaken and the important design results are listed in Table 7.2. By following the step by step procedure, the

Table 7.2 Summary of design calculations for the UCT process operating at 20 days sludge age with an anaerobic sludge mass fraction of 0,15 treating raw and settled wastewaters (Wastewater characteristics given in Tables 4.3, 5.2 and 6.1).

Parameter	Symbol	Units	Raw Wastewater		Settled Wastewater	
Temperature	T	°C	14	22	14	22
Nitrate in r-recycle	N_{nr}	mgN/ℓ	1,0	1,0	1,0	1,0
D.O. in r-recycle	O_r	mgO/ℓ	1,0	1,0	1,0	1,0
Influent biod.COD	S_{bi}	mgCOD/ℓ	492	492	317	317
Rapidly biod.COD fraction	f_{bs}	-	0,24	0,24	0,33	0,33
r-recycle ratio	r	-	1,0	1,0	1,0	1,0
Rapidly biod.COD in anaer.	S_{bsa}	mgCOD/ℓ	53,3	53,3	46,5	46,5
Anaerob.sludge mass	f_{xa}		0,15	0,15	0,15	0,15
Propensity factor	P_f	mgCOD/ℓ	4,24	4,24	3,22	3,22
γ coefficient	γ	mgP/mgVASS	0,246	0,246	0,217	0,217
P removal	P_s	mgP/ℓ	12,2	10,4	6,7	5,6
Effluent P	P_{te}	mgP/ℓ	0,0	0,0	1,8	2,9
Factor of safety	S_f	-	1,25	2,9	1,25	2,9
Max.unaerated sludge mass	f_{xm}	-	0,42	0,42	0,42	0,42
Effluent TKN	N_{te}	mgN/ℓ	3,0	2,0	3,0	2,0
N for sludge production	N_s	mgN/ℓ	13,2	12,6	6,1	5,7
Nitrification capacity	N_c	mgN/ℓ	31,8	33,4	31,9	33,3
Max.anoxic sludge mass	f_{xdm}	-	0,27	0,27	0,27	0,27
Denitrification potential	D_{pp}	mgN/ℓ	29,0	37,3	22,0	27,3
Underflow recycle ratio	s	-	1,0	1,0	1,0	1,0
D.O. in a-recycle	O_a	mgO/ℓ	2,0	2,0	2,0	2,0
D.O. in s-recycle	O_s	mgO/ℓ	1,0	1,0	1,0	1,0
Opt. a-recycle ratio	a_o	-	3,6	5,0*	0,93	2,25
Effluent nitrate	N_{ne}	mgN/ℓ	5,7	4,8	10,9	7,9
UCT process modification						
1st Prim.Anoxic	f_{xd1}	-	0,10	0,10	0,10	0,10
Denitrification potential	D_{pd1}	mgN/ℓ	19,6	21,8	16,0	18,0
Equiv.nitrate load		mgN/ℓ	6,1	4,9	11,3	8,3
Factor of safety	S_{fd}	-	3,2	4,5	1,4	2,2
Modification successful			Yes		Yes	

*The calculated a_o value (i.e. 9,3) is greater than the practical limit of 5. Hence a_o is set equal to the practical limit of 5.

calculations for the raw wastewater at 14°C and 22°C is demonstrated: Accepting an r-recycle ratio to the anaerobic reactor (r) of 1, with 1 mgN/ℓ nitrate (N_{nr}) and 1 mgO/ℓ dissolved oxygen (O_r) (to introduce a factor of safety), the readily biodegradable COD concentration in the anaerobic reactor (S_{bsa}) is found from Eqs (7.1a and 7.2a)

$$\Delta S_{bs} = 1(8,6.1 + 3,0.1) + 3,0.0 = 11,6 \text{ mgCOD}/\ell$$

$$S_{bsa} = \{ 0,24\ (1-0,13-0,05)\ 600 - 11,6\}/(1+1)$$

$$= 53,3 \text{ mgCOD}/\ell.$$

With $f_{xa} = 0,15$, the propensity factor P_f is found from Eq (7.5) i.e.

$$P_f = (53,3-25).0,15 = 4,25 \text{ mgCOD}/\ell.$$

The γ coefficient is found from Eq (7.7) i.e.

$$\gamma = 0,35-0,29\exp(-0,242.4,25)$$

$$= 0,246.$$

With R_s = 20 days, the P removal P_s at 14°C and 22°C is found from Eq (7.6) i.e.

$$P_s = 600\ \{\frac{(1-0,13-0,05)0,45}{(1+0,20.20)}\ (0,246 + 0,015.0,20,0,20.20) + 0,015.0,13/1,48\}$$

$$= 12,2 \text{ mgP}/\ell.$$

and at 22°C

$$P_s = 600\ \{\frac{(1-0,13-0,05)0,45}{(1+0,25.20)}\ (0,246 + 0,015.0,20.0,25.20) + 0,015.0.13/1,48\}$$

$$= 10,4 \text{ mgP}/\ell.$$

As both these removals are greater than the influent P concentration, the effluent P concentration can be taken to be zero.

Accepting a nitrification safety factor (S_f) of 1,25 the maximum unaerated sludge mass fraction at 20 days sludge age, 14°C and μ_{nm20} = 0,36/d is found from Eq (5.32). (Temperature dependency of nitrification constants are given in Table 6.2), i.e.

$$f_{xm} = 1 - 1,25\ (0,034 + 1/20)/0,18$$

$$= 0,42$$

With f_{xm} = 0,42, S_f at 22°C is found from Eq (5.32), i.e.

$$S_f = (1-0,42).0,454/(0,042+1/20)$$

$$= 2,9.$$

Because a reasonable S_f at 14°C has been selected, complete nitrification can be assumed to take place and hence effluent TKN concentration of 3,0 mgN/ℓ at 14°C and 2,0 mgN/ℓ at 22°C are acceptable. The nitrogen requirement for sludge production at 14°C and 22°C is found from Eq (4.23) i.e. 13,2 at 14°C and 12,6 at 22°C. Hence the nitrification capacity N_c is found from Eq (5.33) i.e. 31,8 at 14°C and 33,4 at 22°C.

With f_{xm} and f_{xa} fixed at 0,42 and 0,15 respectively, the maximum anoxic sludge mass fraction (f_{xdm}) is given by Eq (7.8) i.e. f_{xdm} = 0,42 - 0,15 = 0,27. With f_{xdm} = 0,27, the denitrification potential of the primary anoxic reactor with $f_{x1} = f_{xdm}$ = 0,27 is found from Eq (6.20) i.e. 29,0 mgN/ℓ at 14°C and 37,3 at 22°C. With N_c and D_{pp} known and selecting the underflow s-recycle ratio as 1 and the D.O. in the a- and s-recycles (O_a and O_s respectively) as 2 and 1 mgO/ℓ respectively, the nitrogen performance is found from Eqs (6.30 and 6.31) i.e. the optimum a-recycle ratio (a_o) and effluent nitrate concentration (N_{ne}) at 14°C is 3,6 and 5,7 mgN/ℓ respectively and at

22°C the calculated a_o is greater than the practical limit of 5 (i.e. 9,3) so that a_o is set at 5 giving N_{ne} = 4,8 mgN/ℓ (see Table 7.2). For design details of the above procedure see Chapter 6, Section 7.5.

The results in Table 7.2 show that for the *raw wastewater* at 14°C and 22°C, more P can be removed than is present in the influent so that an effluent P concentration of less than 1 mgP/ℓ can be obtained with a factor of safety. The effluent nitrate concentrations are 5,7 mgN/ℓ at 14°C and 4,8 mgN/ℓ at 22°C. Comparing these results with the Phoredox process at 25 days sludge age (Table 7.1), it can be seen that Phoredox process produces a better effluent quality. However, the UCT process incorporates a factor of safety on the P removal whereas the P removal in the Phoredox process depends on the attainment of near complete denitrification without a factor of safety. Consequently, although the UCT process yields a poorer N removal, the P removal can be attained with greater surety in the event of unexpected increases in the TKN/COD ratio. The upper limit of the TKN/COD ratio can be calculated by testing higher TKN/COD ratios on the design and for approximately normal wastewater this is about 0,13.

For the settled wastewater, the P removal (P_s) is 6,7 mgP/ℓ at 14°C and 5,6 mgP/ℓ at 22°C, leaving 1,8 mgP/ℓ and 2,9 mgP/ℓ in the effluent at 14°C and 22°C respectively. The effluent nitrate concentrations (N_{ne}) are 10,9 mgN/ℓ and 7,9 mgN/ℓ at 14°C and 22°C respectively. If P_s is insufficient, then f_{xa} can be increased to its maximum of 0,20, but this will result in a poorer N removal i.e. with f_{xa} = 0,20, P_s = 7,5 mgP/ℓ and N_{ne} = 12,2 mgN/ℓ at 14°C and P_s = 6,4 mgP/ℓ and N_{ne} = 9,7 mgN/ℓ at 22°C. If the N removal with f_{xa} = 0,20 is insufficient, then the sludge age can be increased to improve the N removal but the increase in R_s will reduce the P removal. (see design chart). Clearly there are limits to which biological nutrient removal can be achieved even in an optimally designed process. These limits, and hence the effluent quality, are dependent on the influent wastewater characteristics, in particular the readily biodegradable COD fraction, the TKN/COD ratio and the P/COD ratio i.e. the higher the first and the lower the other two the better the

effluent N and P quality. However, it should be noted that biological N and P removal can be improved by adding readily biodegradable COD to the process (see Chapter 3, Section 3.3). The effect of this external COD addition on the N and P removal in a process can be checked by appropriately adjusting the readily biodegradable COD fraction and influent COD concentration.

Having completed the design for the UCT process, it is necessary to check whether or not the process can be operated as a modified UCT process (Fig 7.6). The conversion to the modified UCT process is done by subdividing the anoxic sludge mass fraction in two subfractions; the first is usually allocated a sludge mass fraction of f_{xd1} of about 0,10, and the second, f_{xd2}, having the remaining sludge mass fraction i.e., $f_{xd2} = f_{xdm} - f_{xd1}$. For successful operation of the modified UCT process, the denitrification potential of f_{xd1} (D_{pd1}) must be greater to its equivalent nitrate load imposed by the underflow s-recycle at the minimum expected temperature T_{min}. The equivalent nitrate load is calculated from the effluent nitrate concentration for the UCT process before subdivision and is given by $s(N_{ne} + O_s/2,86)$. The factor by which D_{pd1} is greater than $s(N_{ne} + O_s/2,86)$ is called the factor of safety (S_{fd}) and it is recommended that this factor be greater than 1,2. (see Section 5 above).

The calculations for the modification of the UCT process treating the raw and settled wastewaters at 20 days sludge age with an anaerobic sludge mass fraction of 0,10 are given in Table 7.2. For both the raw and settled the modification is acceptable - the factor of safety S_{fd} at 14°C for the raw wastewater is 3,2 and for the settled wastewater is 1,4. Generally it will be found that the modification is acceptable for TKN/COD < 0,12 with a readily biodegradable COD fraction (f_{bs}) around 0,25. The TKN/COD ratio limit for successful application of the modification is strongly dependent on the readily biodegradable fraction f_{bs} - the lower the fraction the lower the TKN/COD ratio limit (see Section 5 above). It should be noted also that the magnitude of the anaerobic sludge mass fraction f_{xa}, plays a rôle as to whether or not a UCT process modification will be successful. For example, at 20 days sludge age with $f_{xa} = 0,20$,

the effluent nitrate concentration treating settled wastewater at 14°C is 12,2 mgN/ℓ*, giving an equivalent nitrate load of 12,6 mgN/ℓ; with D_{pd1} = 16,0 mgN/ℓ (see Table 7.2), the factor of safety S_{fd} = 1,26, which is lower than that obtained with f_{xa} = 0,15 (see Table 7.2), and near the limit where the modification would be acceptable.

When checking whether or not the modified UCT process can be successfully applied, it is necessary to check that the first anoxic reactor is sufficiently large to allow complete utilization of the readily biodegradable COD. This is checked by means of Eq (6.22) (see Section 5 above). From Eq (6.22), the minimum anoxic sludge mass fraction to completely utilize the readily biodegradable COD at 14°C is 0,062 and 0,085 for the raw and settled wastewaters respectively (see Table 6.3). Hence f_{xd1} = 0,10 is adequate. By designing f_{xd1} to allow the possibility of complete utilization of the readily biodegradable COD, the modified process can achieve excess P removal up to the TKN/COD ratio at which the effluent nitrate concentration is so high that all the readily biodegradable COD is utilized. This TKN/COD ratio can be calculated by trial and error by testing increasing TKN/COD ratios on the process.

Having made the modification to the UCT process, the possibility of operating it as a UCT process is not excluded; by making provision that the r-recycle flow can be taken from either the first or the second anoxic reactor (see Fig 7.15) the process can be operated either as a modified UCT or a UCT process. The advantages of designing the process as a modified UCT process were set out in detail in Section 2.2.3 above. Furthermore complete flexibility of process operation can be incorporated into the plant by providing optional recycles allowing the plant to be operated as a Modified Phoredox, Modified UCT or UCT process (see Fig 7.17). Also, irrespective of the type of process or combination of processes that are selected for a particular design, it is strongly recommended that the anaerobic reactor is subdivided into three or four compartments and operated in series. The advantage of this series system anaerobic reactor is given in Section 3.4 above.

7.5 Process Volume

The volumes of the reactors of the Phoredox process are calculated by means of the method described in Chapter 6, Section 7.6.1 and for the same sludge sludge age, temperature and COD load, the total volume of a Phoredox process will be the same as that of the Bardenpho process, i.e. subdivision of the process volume between the different reactors

*See page 7.61.

is proportional to the sludge mass fractions of the different reactors. The reactor volumes and retention times for the Phoredox process at 25 days sludge age (see data in Table 7.1) are set out in Table 7.3.

With the UCT process, and its modification the MLSS (or MLVSS) is not uniform throughout the process with the result that the reactor volume fractions are not equal to the sludge mass fractions. There are two methods for determining the volume fractions (or volumes) of the reactors:

i) By calculating the reactor volume fractions from the mass fractions for a fixed total process volume; the anaerobic volume fraction is given by

$$f_{va} = f_{xa} \{(1+r)/(r+f_{xa})\} \qquad (7.10)$$

and the anoxic and aerobic volume fractions are given by

$$f_{vd}/f_{xd} = f_{vb}/f_{xb} = 1 - \{f_{xa}/(r+f_{xa})\} \qquad (7.11)$$

where
first subscript v and x refer to volume and mass fractions respectively and second subscripts a,d and b refer to anaerobic, anoxic and aerobic reactors respectively.

Knowing the volume fractions, the volumes of the reactors are calculated from the total volume of the process for a selected mean process MLSS concentration $\bar{X}_t$ (see Eq 4.16). For the selected mean MLSS concentration $\bar{X}_t$, the MLSS concentrations in the reactors are given by the following equations; in the anaerobic reactor (X_{ta}),

$$X_{ta} = \bar{X}_t . f_{xa}/f_{va} \qquad (7.12)$$

in the anoxic (X_{td}) and aerobic (X_{tb}) reactors

$$X_{td} = X_{tb} = \bar{X}_t/[1-\{f_{xa}/(r+f_{xa})\}] \qquad (7.13)$$

Table 7.3 Reactor volumes and nominal and actual retention times for the Phoredox process treating raw and settled wastewaters at 25 days sludge age. For process performance see Table 7.1.

Process Parameter	Symbol	Wastewater		Units
		Raw	Settled	
Sludge Mass	$M(X_t)$	54200	21850	kgTSS
Average MLSS conc.	$\bar{X}_t$	4000	4000	mg/ℓ
Total volume	V_p	13550	5460	m³
Total flow	Q	13330	13330	m³/d
Total nom.ret.time	R_{ht}	24,4	9,8	hr
Mixed liq. recycle (14°C)	a	3,3	1,3	-
Underflow recycle	s	1,0	1,0	-
Anaerobic				
Mass fraction	f_{xa}	0,10	0,10	
Volume		1355	546	m³
Nom.ret.time		2,4	1,0	hr
Actual ret.time		1,2	0,5	hr
Primary Anoxic				
Mass fraction	f_{x1}	0,16	0,26	
Volume		2168	1420	m³
Nom.ret.time		3,9	2,6	hr
Actual ret.time		0,74	0,79	hr
Main Aeration*				
Mass fraction		0,45	0,45	
Volume		6098	2457	m³
Nom.ret.time		11,0	4,4	hr
Actual ret.time		2,1	1,34	hr
Secondary Anoxic				
Mass fraction	f_{x3}	0,24	0,14	
Volume		3252	764	m³
Nom.ret.time		5,9	1,4	hr
Actual ret.time		2,9	0,7	hr
Reaeration*				
Mass fraction		0,05	0,05	
Volume		678	273	m³
Nom.ret.time		1,2	0,50	hr
Actual ret.time		0,6	0,25	hr

*The reaeration reactor is usually taken to have a sludge mass fraction of 0,05 to 0,07 and this fraction is deducted from the aerobic sludge mass fraction; the remaining aerobic sludge mass fraction constitutes the main aeration sludge mass fraction.

From Eq (7.13), it can be seen that the sludge concentration in the anoxic (X_{td}) and aerobic (X_{tb}) reactors is greater than the selected mean concentration $\bar{X}_t$. For r = 1 and f_{xa} = 0,15, X_{td} and X_{tb} are 15% higher than $\bar{X}_t$. This higher than mean aerobic reactor sludge concentration must be taken into account in the design of the secondary settling tanks, which receive the outflow from the aerobic reactor.

ii) By calculating the reactor volumes from the sludge mass fractions for a fixed aerobic reactor sludge concentration X_{tb}; if the anaerobic sludge mass fraction is f_{xa}, then the remaining sludge $(1-f_{xa})MX_t$, is diluted into the anoxic and aerobic reactors i.e. the combined volumes of the anoxic and aerobic reactors is given by $(1-f_{xa})MX_t/X_{tb}$. The subdivision of this volume is easily found from their sludge mass fractions because the sludge concentrations in these reactors are t same. Now the sludge concentration in the anaerobic reactor X_{ta} is a fraction r/(1+r) of the concentration in the aerobic reactor i.e. $X_{ta} = X_{tb}\ r/(1+r)$. Knowing the mass of sludge in the anaerobic reactor i.e. $f_{xa}\ MX_t$, and the concentration X_{ta} the volume is given by $f_{xa}\ MX_t/X_{ta}$. This method will yield a larger process volume than method (i) for the same aerobic reactor sludge concentration X_{tb}.

Comparing the volumes of the UCT process attained with the above two methods with volume of the Phoredox process, method (i) will produce a process volume equal to that of the Phoredox for the same mean process concentration $\bar{X}_t$ but the aerobic reactor sludge concentration in the UCT process will be greater than that in the Phoredox {by a factor $(1+f_{xa})$}, and method (ii) will produce a process volume larger than that of the Phoredox {by a factor $(1+f_{xa})$} for the same aerobic reactor sludge concentration. Reactor volumes, retention times for the UCT process as found from method (ii) are given in Table 7.4.

7.6 Oxygen Demand

The average daily oxygen demand for a nitrogen and phosphorus removal process is calculated in the identical fashion as that for a nitrogen removal process. This is discussed in detail in Chapter 6, Section 7.6.2.

Table 7.4 Reactor volumes and nominal and actual retention times for the modified UCT process treating raw and settled wastewaters at 20 days sludge age. For process performance see Table 7.2.

Process Parameter	Symbol	Wastewater		Units
		Raw	Settled	
Sludge mass	$M(X_t)$	54200	21850	kgTSS
Aerobic reactor MLSS conc.	X_{tb}	4000	4000	mgTSS/ℓ
Anaerobic sludge fraction	f_{xa}	0,15	0,15	-
Anaerobic sludge mass		8130	3278	kgTSS
Anoxic + Aer. sludge mass		46070	18572	kgTSS
Anoxic + Aer. volume		11518	4643	m³
Total anoxic sludge fraction	f_{xdm}	0,27	0,27	
First primary anoxic	f_{xd1}	0,10	0,10	
Second primary anoxic	f_{xd2}	0,17	0,17	
Aerobic sludge mass fraction	f_{xb}	0,58	0,58	
1st Anoxic volume		1355	546	m³
2nd Anoxic volume		2304	1475	m³
Aerobic volume		7860	3168	m³
r-recycle ratio	r	1	1	
Anaerobic MLSS conc.	X_{ta}	2000	2000	mgTSS/ℓ
Anaerobic volume		4065	1639	m³
Total volume		15583	6282	m³
Average process conc.	$\bar{X}_t$	3480	3480	mgTSS/ℓ
Opt.a-recycle ratio	a_o	3,6	0,93*/1,5**	
Underflow recycle ratio	s	1,0	1,0	
Influent flow	Q	13330	13330	m³/d
Retention times				
Anaerobic : Nominal		7,3	3,0	hr
Actual		3,6	1,5	hr
1st Anoxic: Nominal		2,4	1,0	hr
Actual		0,8	0,3	hr
2nd Anoxic: Nominal		4,1	2,7	hr
Actual		0,9	1,4*/1,1**	hr
Aerobic : Nominal		14,2	5,7	hr
Actual		3,1	3,0*/2,3**	hr

* Based on the calculated optimum mixed liquor recycle ratio a_o.
** Based on a mixed liquor recycle ratio to yield an actual anoxic retention time of about 1 hour.

A simple design rule by means of which the average peak daily oxygen demand can be estimated from the influent COD and TKN load variation over the day is also given in this section.

8. GUIDELINES FOR PROCESS SELECTION

From the theory of biological excess P removal and the nitrogen removal behaviour of the various processes, the following broad guidelines can be given to assist the selection of a process:

8.1 Process Selection

1) If the readily biodegradalbe COD concentration in the influent (S_{bsi}) is less than 60 mgCOD/ℓ (irrespective of the influent COD concentration), significant excess P removal is unlikely to be obtained in any of the processes.

2) If S_{bsi} > 60 mgCOD/ℓ, excess P removal can be achieved provided nitrate can be excluded from the anaerobic reactor, the removal increasing as S_{bsi} increases. Whether or not nitrate can be excluded from the anaerobic reactor depends on the influent TKN/COD ratio and the process type. The limits* given below are for approximately normal wastewaters, (eg. with readily biodegradable COD fraction f_{ts} around 15 to 20%) and where complete nitrification is obligatory**

   i) If the TKN/COD < 0,08 mgN/mgCOD, complete nitrate removal is possible and the Phoredox process is indicated.

   ii) If 0,08 < TKN/COD < 0,11 complete nitrate removal no longer is possible, but nitrate can be excluded from the anaerobic reactor by using the modified UCT process.

   iii) If 0,11 < TKN/COD < 0,14, the modified UCT process no longer can exclude nitrate from the anaerobic reactor and the UCT process is indicated provided the a-recycle ratio is carefully controlled. However, poor settling sludges may be encountered.

   iv) If TKN/COD > 0,14 it is unlikely that biological excess P removal will be achieved with normal municipal wasteflows.

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* Generally, the higher the f_{ts} ratio above 0,20, the higher these limits and the lower the f_{ts} ratio below 0,20 the lower these limits. These different limits can be calculated with the theory present in this monograph using different f_{ts} ratios.

**In South Africa, complete nitrification is obligatory. Where complete nitrification not obligatory, nitrate discharge to the anaerobic reactor can be avoided by limiting n rification by e.g. limiting the oxygen supply to the process, but in South Africa, such strategy falls in line more with an emergency action than a design criterion.

8.2 Anaerobic Sludge Mass Fraction Selection

The readily biodegradable COD fraction (f_{ts}) is approximately 0,20 for raw municipal wastewaters (i.e. f_{bs} about 0,25), and approximately 0,30 for settled municipal wastewaters (i.e. f_{bs} about 0,34) - see Table 6.2 and Chapter 3, Section 3. Consequently, for approximately normal municipal wastewaters, the lower the COD strength (S_{ti}) the lower the S_{bsi}, when S_{ti} for raw wastewater is less than 250 mgCOD/ℓ, S_{bsi} is less than 50 mgCOD/ℓ and the attainment of excess P removal for r or s-recycle ratios of 1:1 is unlikely or sporadic even if the process is correctly selected and designed. Conversely the higher the S_{ti}, the greater the S_{bsi} and the easier it is to establish the conditions for excess P removal and obtain high P contents in the active mass of the sludge γ. As γ is related to both (S_{bsa}-25) and the anaerobic sludge mass fraction f_{xa}, the adverse effect of low (S_{bsa}-25) at low S_{ti} can be countered to a degree by increasing f_{xa} to its maximum* of 0,20.

The following guidelines based on raw COD strengths are not unreasonable for an initial estimate of f_{xa} to obtain good excess P removals for approximately normal municipal wastewaters:

i) $S_{ti} < 400$ mgCOD/ℓ, $f_{xa} = 0,20$

ii) $400 < S_{ti} < 700$, $f_{xa} = 0,15$

iii) $S_{ti} > 700$ mgCOD/ℓ $f_{xa} = 0,10$

The above initial estimates must be checked and modified depending on the actual P/COD and readily biodegradable COD fraction.

8.3 Subdivision of Anaerobic Reactor

Recent research has indicated that it is advantageous to subdivide the anaerobic reactor into a number of compartments operated in series. This is because the absorption of readily biodegradable COD by the poly-P accumulating organisms appears to be a first order reaction (see Section 3.4 above) so that, for the same anaerobic sludge mass fraction, a series of completely mixed reactors operates more effectively than a single

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* See footnote page 7.40.

completely mixed reactor. Theoretically, the greater the number of equal volumed compartments the better, but practically very little advantage is gained by having more than 3 to 4. Four compartments would appear to be the most suitable because then, by providing the required additional recycle flows, the process can be operated as a Modified Phoredox or UCT type process each with approximately the same anaerobic sludge mass fraction (see Fig 7.17).

9. CLOSURE AND CONCLUSIONS

The above calculations demonstrated that:

1) The average wastewater characteristics govern the design of and the effluent quality attainable in an activated sludge process for biological N and P removal. The principal wastewater characteristics are:

   (i) the COD concentration (S_{ti})
   (ii) the readily biodegradable COD fraction (f_{ts})
   (iii) the TKN/COD ratio
   (iv) the maximum specific growth rate of the nitrifiers at 20°C (μ_{nm20})
   (v) the maximum and minimum temperatures (T_{max}) and T_{min})
   (vi) the P/COD ratio.

2) Once the sludge age of a selected process is fixed the removals of N and P attainable are fixed and the N and P removal *efficiencies* then depend on the TKN/COD and P/COD ratios of the wastewater. Because for approximately normal wastewaters (f_{ts} = 0,20) complete denitrification can only be achieved for the TKN/COD ratios less than 0,08 (without the addition of an external energy source), the higher the ratio above 0,08, the lower N removal efficiency.

3) Attainment of excess P removal is crucially dependent on the readily biodegradable COD concentration in the influent S_{bsi}. For recycle ratios to the anaerobic reactor of 1:1, if S_{bsi} < 50 mgCOD/ℓ, it is highly unlikely that excess P removal can be achieved in any process; if S_{bsi} < 50 mgCOD/ℓ, excess P removal can be achieved provided nitrate can be excluded from the anaerobic reactor, in which event, the degree of excess P removal depends on the magnitude of S_{bsi} above 50 mgCOD/ℓ and the influent COD strength S_{ti}. The sensitivity of excess P removal to the S_{bsi} concentration is such that any practice that reduces S_{bsi} should be avoided (see Chapter 3, Section 3) and conversely, any practice which increases S_{bsi} should be encouraged (see Chapter 3, Section 3 and Chapter 6, Section 7.1.3).

4) In general, the establishment of a readily biodegradable COD concentration in the anaerobic reactor (S_{bsa}) in excess of 25 mgCOD/ℓ, to stimulate excess P removal, becomes increasingly more difficult as the raw influent COD strength of the wastewater (S_{ti}) decreases: For average readily biodegradable COD fractions ranging between 0,20 to 0,25, the minimum S_{ti} for which S_{bsa} is greater than 25 mgCOD/ℓ is about 250 mgCOD/ℓ; as S_{ti} increases above 250 mgCOD/ℓ, the establishment of S_{bsa} greater than 25 mgCOD/ℓ becomes increasingly easier and the excess P removal per unit influent COD increases and the attainment of excess P removal becomes less sensitive to external factors, e.g. D.O. control in the process.

5) Cyclic flow and load conditions do not appear to affect the mean daily excess P removal, in fact, the removal often is improve, particularly under low average influent COD conditions. The reason for this improvement is that under the cyclic conditions (with constant recycle flows) during the peak periods the peak COD is higher than the daily mean causing a higher (S_{bsa}-25) condition and hence higher P removals during the associated high flow period. However, under cyclic flow conditions the D.O. concentration in the aerobic reactor must be closely controlled; too high D.O. concentration reduces the nitrate removal whereas too low concentration may inhibit nitrification, inhibit excess uptake of P and adversely affect settling. The practical difficulties associated with oxygen control are such that serious consideration should be given to equalization tanks operated under a control strategy that equalizes *both* flow and load. Such a strategy is now available (Dold, Buhr and Marais, 1982) (see Chapter 10 on the operation of nutrient removal processes).

6) For successful excess P removal in the Phoredox process, near complete denitrification must be achieved to avoid excessive nitrate discharge to the anaerobic reactor. Complete denitrification can be achieved only for TKN/COD ratios < 0,08 mgN/mgCOD for readily biodegradable COD fractions (f_{ts}) of 0,20 at 14°C. For TKN/COD ratios > 0,08* mgN/mgCOD, complete denitrification is unlikely to be achieved and the indicated processes for obtaining excess P removal are the UCT type processes.

7) In the UCT type processes, by appropriate control of the mixed liquor a-recycle, the anaerobic reactor can be protected against nitrate discharge for TKN/COD ratios up to 0,14 mgN/mgCOD even though nitrate will be present in the effluent. For TKN/COD ratios < 0,11, the

* See footnotes pages 7.68 and 7.73.

modified UCT process can achieve excess P removal and has the advantage over the UCT process of less need for operator intervention and is more likely to maintain reasonably good sludge settling characteristics. For TKN/COD ratios > 0,11 mgN/mgCOD, the only process that can achieve excess P removal is the UCT process, but it is possible that rather poor sludge settling characteristics will be obtained if the influent COD is high.

8) For TKN/COD ratios > 0,14 mgN/mgCOD, it is unlikely that biological excess P removal can be obtained when complete nitrification is obligatory due to the inability to achieve sufficient denitrification without the addition of an external energy source. However, such high TKN/COD ratios are unlikely to be encountered in raw or settled municipal wastewaters.

9) Primary sedimentation is unfavourable for achieving high removals of both N and P because it significantly increases the TKN/COD and P/COD ratios and significantly reduces the COD strength of the wastewater although the readily biodegradable COD concentration is only marginally affected. However, primary sedimentation significantly reduces the process volume requirements and total oxygen demand.

10) For design of nutrient removal plants the influent wastewater characteristics (or their ranges) need to be known with much greater surety than for conventional activated sludge plants otherwise a design may be produced that fails totally in its P removal objectives. Vital influent characteristics are listed in (1) above. Useful data are the Total Alkalinity and the unbiodegradable COD fractions f_{us} and f_{up}. In the event that the vital characteristics are known only approximately, values should be selected that lead to conservative designs, usually at the cost of reduced N and P removal.

11) The selected process must have factors of safety built into it or have flexibility in operation, so that if the influent characteristics are more adverse than accepted for design, it will be possible to accommodate them. For example, if a Phoredox process is selected it is recommended that normally the maximum TKN/COD ratio should not

exceed 0,07† mgN/mgCOD and the process should have a built-in safety factor by designing it for 0,08† mgN/mgCOD. For TKN/COD ratios > 0,07† mgN/mgCOD, the Phoredox/modified UCT/UCT process should be selected; with this process combination, by appropriate regulation of the recycles, excess P removal can be induced (subject to S_{bsi}). Theoretically, at low TKN/COD ratios ($\cong$0,08†), the Phoredox process will be the optimal one, but practically its inflexibility to accommodate TKN/COD ratio variations which exceed 0,08 is a disadvantage. With the modified UCT/UCT process excess P removal can be obtained (subject to S_{bsi}) at the expense of N removal. By providing the various optional recycles, the best results can be obtained when required during the life of the plant.

12) The selected process should require the least amount of decision making from the operator to obtain consistent results. In this regard the modified UCT/UCT process* appears to lend itself most readily to setting operational procedures to absorb adverse conditions when these arise. Also operational adjustment to mitigate the regular changes in wastewater flow and characteristics observed over different days of the week can be preprogrammed.

10. REFERENCES and BIBLIOGRAPHY

1. Barnard J L (1975a). Biological nutrient removal without the addition of chemicals. Water Research, 9, 485-490.

2. Barnard J L (1975b). Nutrient removal in biological systems. Wat.Pollut.Control, 74, 2, 143-154.

3. Barnard J L (1976). A review of biological phosphorus removal in the activated sludge process. Water S A., 2, 3, 136-144.

4. Dold P L, G A Ekama and G v R Marais (1980). A general model for the activated sludge process. Prog.Wat.Tech., 12, 47-77.

5. Dold P L, H O Buhr and G v R Marais (1982). Design and Control of Equalization Tanks. Research Report No W 42, Dept.of Civil Eng., University of Cape Town.

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†These values are valid for a readily biodegradable COD fraction (f_{bs}) of 0,24. Generally the higher (lower) the fraction, the higher (lower) these limits.

*See Sections 5, 7.4 and 8.3 above.

6. Ekama G A, I P Siebritz ana G v R Marais (1982). Considerations in the process design of nutrient removal activated sludge processes. Presented at the IAWPR post-Conf.seminar on Phosphate removal, Pretoria, April 1982. Procs. to be published in Wat.Sci.Tech.

7. Ekama G A, A C van Haandel and G v R Marais (1979). The present status of research on nitrogen removal : a model for the modified activated sludge process. Presented at the Symposium on Nutrient Removal, S A Branch of IWPC Pretoria, May 1979. Proceedings published by Water Research Commission of South Africa.

8. Fuh G W and Min Chen (1975). Microbiological basis of phosphate removal in the activated sludge process for the treatment of wastewater. Microbial Ecology, 2, 119-138.

9. Florentz M and P Granger (1982). Phosphorus 31 nuclear magnetic resonance of activated sludge use for the study of the biological removal of phosphates from wastewater. Submitted for publication to *Biochemical and Biophysical Research Communications*.

10. Hoffman R and G v R Marais (1977). Phosphorus removal in the modified activated sludge process. Research report W 22, Dept. of Civil Eng., Univ. of Cape Town.

11. Law S M, P L Dold and G v R Marais (1982). Phosphate release and uptake by activated sludge in batch experiments. Research Report W 44 Dept.of Civil Eng., University of Cape Town.

12. Marais G v R and G A Ekama (1976). The activated sludge process Part I - steady state behaviour. Water S.A., 2, 4, 163-200.

13. Marais G v R, R E Loewenthal and I P Siebritz (1982). Review: Observations supporting phosphorus removal by biological uptake. Presented at IAWPR post-Conf.seminar on Phosphate removal, Pretoria. Procs. to be published in Wat.Sci.Tech.

14. Marsden M G and G v R Marais (1977). The rôle of the primary anoxic reactor in denitrification and biological phosphorus removal. Research Report W 19, Dept.of Civil Eng., University of Cape Town.

15. Martin K A C and G v R Marais (1975). Kinetics of enhanced phosphorus removal in the activated sludge process. Research Report W 14, Dept.of Civil Eng., University of Cape Town.

16. McLaren A R and R J Wood (1976). Effective phosphorus removal from sewage by biological means. Water S A., 2, 1, 47-50.

17. Nicholls H A (1975). Full scale experimentation on the new Johannesburg extended aeration plant. Water S A., 1, 3, 121-132.

18. Nicholls H A (1978). Kinetics of phosphorus transformations in aerobic and anaerobic environments. Presented at 9th IAWPR post conf. seminar, Copenhage, Prog.Wat.Tech.,10.

19. National Institute of Water Research (NIWR) interim design guide for the modified activated sludge process.

20. Nicholls H A (1982). Application of the Marais-Ekama activated sludge model to large plants. Presented at 11th IAWPR Conf. Cape Town. Proceedings to be published in Wat.Sci.Tech.

21. Nicholls H A, D W Osborn and G v R Marais (1982). Performance of large scale nutrient removal activated sludge plants. Research Report W 43, Dept.of Civil Eng., University of Cape Town.

22. Rabinowitz B and G v R Marais (1980). Chemical and biological phosphorus removal in the activated sludge process. Research Report W 32, Dept.of Civil Eng., University of Cape Town.

23. Rensink J H (1981). Biologische defosfatering en processbepalende faktoren. In Symp.Book - Defosfatering niewe ontwikkelingen en praktijkervaringen in Nederland and Zweden. NVA Symp. (in Dutch).

24. Siebritz I P, G A Ekama and G v R Marais (1980). Excess Biological Phosphorus removal in the Activated Sludge Process at Warm Temperate Climates. Proc. Waste Treatment and Utilization, Vol.2, 233-251, Eds C W Robinson, M Moo-Young and G J Farquhar, Pergamon Press, Toronto.

25. Siebritz I P, G A Ekama and G v R Marais (1983). Biological phosphorus removal in the activated sludge process. Research Report W 46, Dept. of Civil Eng., University of Cape Town.

26. Siebritz I P, G A Ekama and G v R Marais (1982). A parametric model for biological excess phosphorus removal. Presented at the IAWPR post-Conf. seminar on phosphate removal, Pretoria. Procs. to be published in Wat.Sci.Tech.

27. Simpkins M J and A R McLaren (1978). Consistent biological phosphate and nitrate removal in an activated sludge plant. Prog.Wat.Tech., 10, 5/6, 433-442.

28. Stern L B and G v R Marais (1974). Sewage as the electron donor in biological denitrification. Research Report W 7, Dept.of Civil Eng., University of Cape Town.

29. Wilson D E and G v R Marais (1976). Adsorption phase in biological denitrification. Research Report W 11, Dept.of Civil Eng., University of Cape Town.

CHAPTER EIGHT

SECONDARY SETTLING TANKS

by

G A Ekama, A R Pitman, M Smollen and G v R Marais

1. INTRODUCTION

In the activated sludge process, it is necessary to separate the treated wastewater from the biological sludge mass thereby producing a clear final effluent. This solid/liquid separation phase is traditionally achieved by gravity sedimentation tanks although flotation has also been shown to be feasible.* Only solid/liquid separation by gravity sedimention in secondary settling tanks will be considered in this chapter.

The secondary settling tank is a vital part of the activated process. It combines the function of a clarifier (producing a clarified final effluent) and a thickener (producing a continuous underflow of thickened sludge for return to the biological reactor) (Fig 8.1). Should the settling tank fail in either of these two functions, sludge will be carried over the effluent weirs and escape with the effluent. Besides delivering an effluent of poor quality, loss of sludge could affect the behaviour of the biological process by uncontrolled reduction of the sludge age to values below that required for proper plant performance, for example, if the sludge age is reduced to below that required for nitrification, nitrogen removal by denitrification will cease.

The conditions in the biological reactor affect the settling and clarification characteristics of the sludge. For example, under aeration reduces the settleability of the sludge; over aeration may lead to pin-flock formation and poor clarification even though the sludge maintains good settling characteristics and often in processes where large proportions of the sludge are intentionally unaerated as in nutrient removal processes, poor settling characteristics are encountered. Thus, the functions of the biological process and that of the

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*A design guide for solid/liquid separation and waste sludge thickening is available (Bratby and Marais, 1976, 1977).

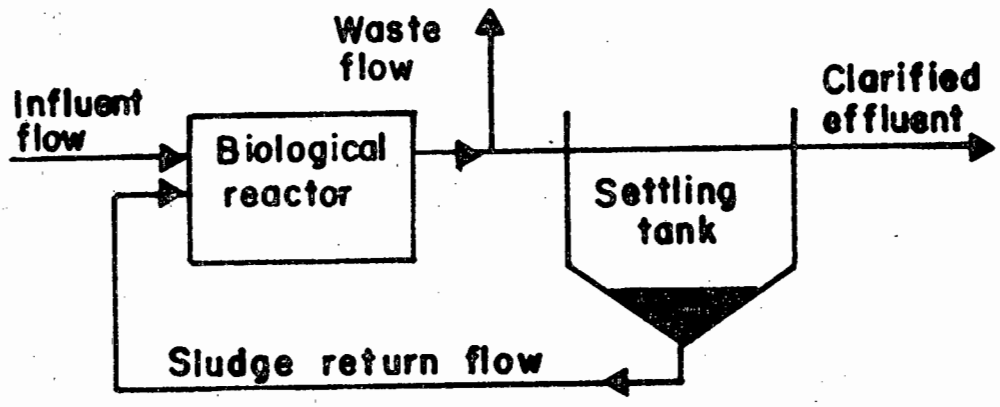

Fig 8.1 The activated sludge process incorporating the secondary settling tank for liquid-solid separation.

secondary settling tank interact upon eachother and the design of the one cannot be undertaken independently of the other - failure in either of these two unit processes causes failure of design objectives.

The settling characteristics of the sludges in activated sludge processes differ widely between different process types and also vary with time in the same process depending on the composition of the influent (see Section 7 below). For the various types of wastewaters and sludges to be treated, the design procedures for the secondary settling tanks have tended to be of an *ad hoc* nature - for each type of sludge, design rules were set down that experience has shown will provide generally for adequate

functioning of the settling tank over the range sludge settling behaviour that was found could arise. These rules often do not *directly* incorporate the settling characteristics of the sludge - these are lumped together with the hydraulic characteristics, as illustrated by the design rules taken from the IWPC designers handbook.* (1) the overflow rate must not exceed 1 $m^3/m^2/h$ at Peak Wet Weather Flow (PWWF) (2) the retention time must not be less than 1,5 h at Peak Dry Weather Flow (PDWF) (3) maximum discharge per unit length of effluent weir 8,3 $m^3/h/m$. These design rules implicity accept that the sludge settling characteristics will not fall below a certain minimum quality, a quality unknown but in conformity with past experience of similar sludges. Where processes are developed that generally tend to affect the settling characteristics adversely these rules may result in inadequate designs resulting in failure of the settler and the process.

Considerable research has been undertaken in unravelling the behaviour of secondary settling tanks and to develop a reliable design procedure that recognizes the settling characteristics of the sludge. However, the settling process is complex and the factors affecting settling so many that general procedures for design have not emerged. This is principally the case with activated sludge where constituents in the influent wastewater or conditions imposed on the process may radically change the settling characteristics of the sludge, and *ad hoc* rules specific only to certain categories of sludge have tended to be the usual method.

Lack of understanding of settling behaviour in settling tanks, and of its interaction with the process in both design and operation has been the source of considerable difficulties in the operation of activated sludge processes in South Africa. The first indication of failure has nearly always been a loss of sludge over the effluent weirs of the settling tank. This loss of sludge does not necessarily imply that the settling tank is at fault; the conditions in the biological reactor may have caused a deterioration in the settling characteristics of the sludge.

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*"Guide to the design of sewage purification works" prepared by the IWPC.

The design of the secondary settling tank based on the settling characteristics of the sludge and the interaction between the secondary settling tank and biological process are briefly discussed in this chapter.

2. SECONDARY SETTLING TANK DESIGN

The settling tank performance is not only governed by the overflow rate (clarification function) but also by the transmission of the applied solids to the bottom of the tank (thickening function). These two functions operate simultaneously but usually either one or the other will be critical during the daily cyclic operation of the settling tank. Conventional design procedures by specifying only an overflow rate in effect tend to provide mainly for the clarification function. In contrast although research has been devoted to thickening, design criteria for thickening have not been developed to a large degree.

Earlier research into thickening has been mainly undertaken with non flocculant suspensions (e.g. Coe and Clevenger, 1916 and Kynch, 1952). These investigations have established the importance of the mass flux approach. Although activated sludge is a flocculant suspension, it has been shown that the mass-flux concept also can be applied to activated sludge (Dick, 1970 and 1972). Application of the mass flux concept to the settling tank design has been particularly assisted by the graphical method of Yoshioka et al (1957), which allows estimation of the settling tank area for the thickening function (see Section 5.1 below).

The mass flux approach requires the measurement of the change in settling velocity of the sludge with change in sludge concentration as the sludge settles and thickens in the bottom of the settling tank. A method of assessing the settling behaviour of the sludge in the bottom of the tank is by means of the stirred batch settling test.

3. STIRRED BATCH SETTLING TEST

Mixed liquor from activated sludge plants usually show a strong flocculating tendency and even at low concentrations (1000mg MLSS/ℓ) exhibit a zone settling mode. In the zone settling mode, the concentration of sludge is such that the particles irrespective of size, all

tend to settle at the same rate throughout the zone depth. The rate of settling is controlled by the rate at which the water passes upward through the mass and this is inversely related to the concentration. Although the mass settles as an entity leaving a clear liquid-mixed liquor interface, the particles are supported by the water between the particles, i.e. upper particles are not mechanically supported by lower ones.

Compression is observed at the bottom of the batch settling test. In the compression region each layer of particles provides mechanical support to the layers above it. Particle movement no longer is governed only by hydraulic frictional forces and the links between the particle. Forces transmitted by particle contact via the compressible properties of the sludge and the interstitial pressure caused by the squeezing out of water from the compressing particles govern the settling behaviour in the compression stage.

Consider a batch settling test tube filled with sludge of concentration such that zone settling commences immediately (see Fig. 8.2). Initially the concentration is uniform throughout and region B occupies the total depth (8.2a). Immediately after settling commences, a solid-liquid interface develops and a region of clarified liquid A is formed (8.2b). In region B the particles still settle at uniform velocity under zone settling conditions, and throughout region B the concentration is constant. The interface settling velocity is a constant value and is a function of the concentration of region B, which is the same as the MLSS concentration at the start of the test. Similtaneously with the formation of region A, regions C and D are formed. Region D is one in which compression occurs and region C is the transition stage from zone settling to compression. Region C is still a zone settling region but the concentration increases down the zone. In a particular test, the transition zone depth generally is considered to remain constant until the solid-liquid interface reaches it.

A plot of the solid-liquid interface height versus time is given in Fig. 8.3. The interface settling velocity is slow initially

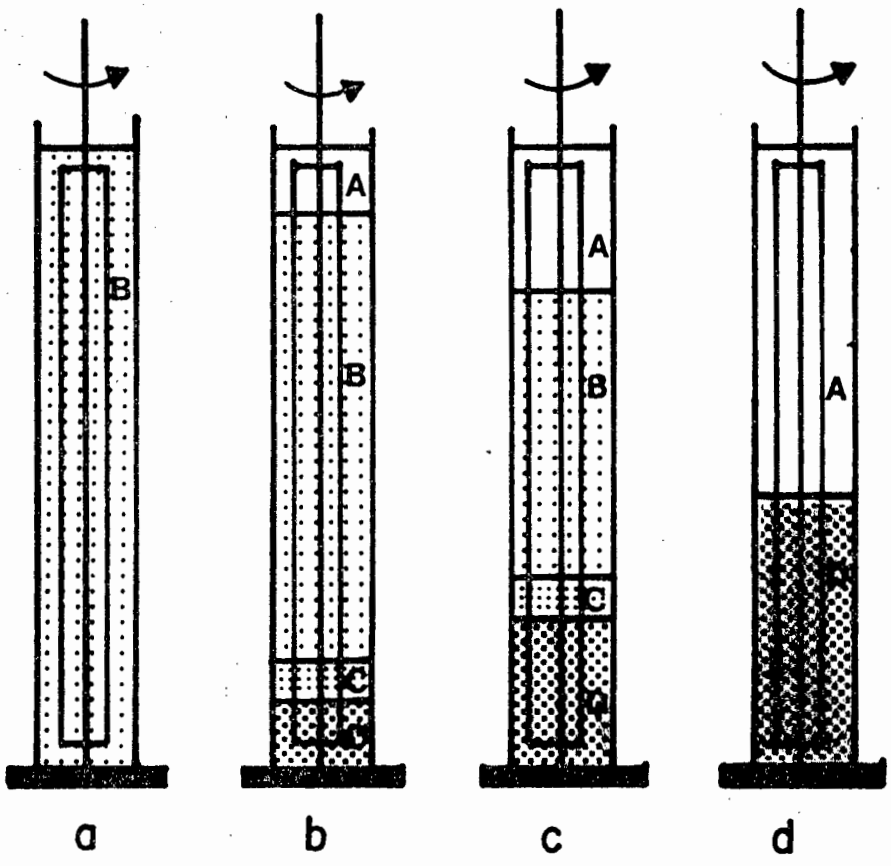

Fig 8.2 Chronological progress of a stirred batch settling test.

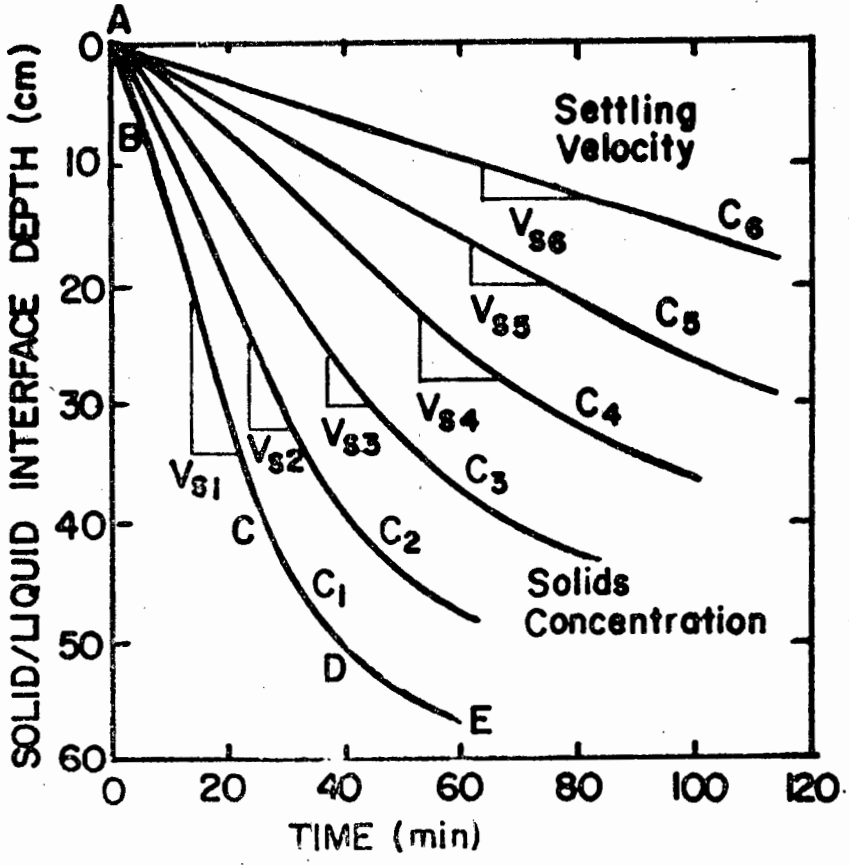

Fig 8.3 Solid-liquid interface height versus time observed in batch settling tests at different initial solids concentrations.

(A-B) because the activated sludge requires some time to reflocculate from the disturbance of the sludge flocs during the filling of the test cylinder. To minimize this effect, it is necessary to fill the test cylinder from the bottom as slow as practically possible so as to cause minimal disruption of the sludge flocs. After a time a constant interface velocity is observed (B-C) until region B sinks into region C. Thereafter the interface velocity decreases as denser and denser concentrations appear at the interface due to the subsidence of the less dense layers into the denser ones, until the compression region D is reached. Thereafter subsidence continues but now the velocity is governed by the compression behaviour of the sludge.

The interface velocity of the constant concentration zone settling region is given by the slope of line B-C in Fig. 8.3. This velocity is defined as the settling velocity (V_s) of the sludge at the concentration equal to that of the uniform concentration in the test cylinder at the start of the test (X). The settling velocity V_s decreases as the sludge concentration increases (X) (Fig. 8.3).

4. SOLIDS FLUX

Solids flux is defined as the product of the settling velocity V_s and the concentration of the sludge, i.e.

$$G_s = V_s X \qquad (8.1)$$

G_s = solids flux ($kg/m^2/d$)

V_s = settling velocity (m/d)

X = sludge concentration ($kgMLSS/m^3$)

By conducting a number of batch settling tests, the flux at different sludge concentrations can be determined. A typical flux curve for activated sludge is shown in Fig. 8.4 in which solids flux (G_s) is plotted versus sludge concentration (X). At low X, although V_s is high the product G_s is low. At high X, V_s is low also giving a low G_s. At some intermediate X (about 3 to 5 kg/m^3 for activated sludge), G_s is a maximum.

5. GRAPHICAL APPLICATION OF FLUX THEORY

5.1 Graphical Procedure

In continuous settling tank operation (shown schematically in Fig. 8.5), the sludge entering the settler is transferred to the bottom by two flux components (1) the gravity flux (G_s) and (2) the flux caused by the downdraft flow generated by the sludge abstraction flow from the bottom of the settler, called the bulk flux. The gravity flux is given by Eq (8.1). The bulk flux (G_b) is the product of the sludge concentration X and the underflow velocity (U_u) where the underflow velocity is the downdraft velocity caused by the underflow sludge abstraction i.e.

$$G_b = U_u X \qquad (8.2)$$

and

$$U_u = Q_r/A \qquad (8.3)$$

where

U_u = underflow velocity (m/d)

Q_r = underflow rate (m^3/d)

A = surface area of settling tank (m^2)

For a fixed underflow rate, the bulk flux is proportional to the sludge concentration. This is depicted graphically in Fig. 8.6.

The total flux (G_t) to the bottom of the settler is the sum of the two flux components i.e.

$$G_t = G_s + G_b$$

$$= X (V_s + U_u) \qquad (8.4)$$

For a selected value of the underflow velocity U_u (i.e. Q_r and A), the two flux components can be added graphically (see Fig. 8.7). For the particular choice of U_u, the total flux G_t attains a minimum value G_1 at a concentration X_1, and this minimum limits the rate at which sludge can reach the bottom of the settling tank. Hence to ensure that all the sludge reaches the bottom, the sludge mass applied to the settling tank per unit surface area i.e. the applied flux (G_{ap}) must be equal or less than the limiting flux (G_1). The applied flux

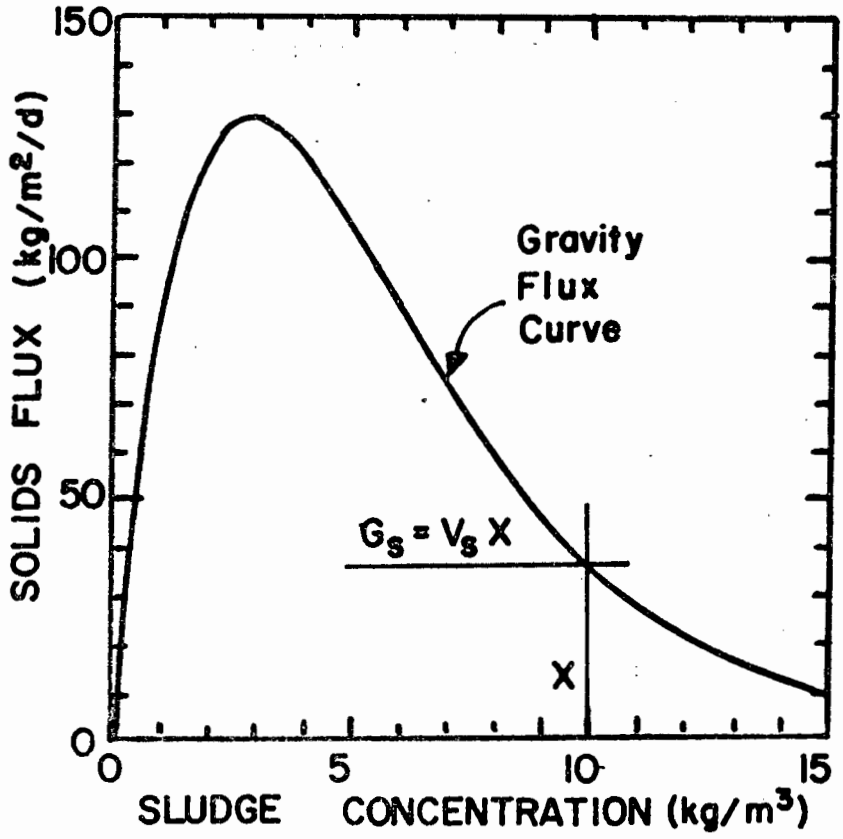

Fig 8.4 The gravity solids flux versus sludge concentration curve, i.e. downwards sludge transport due to gravity sedimentation.

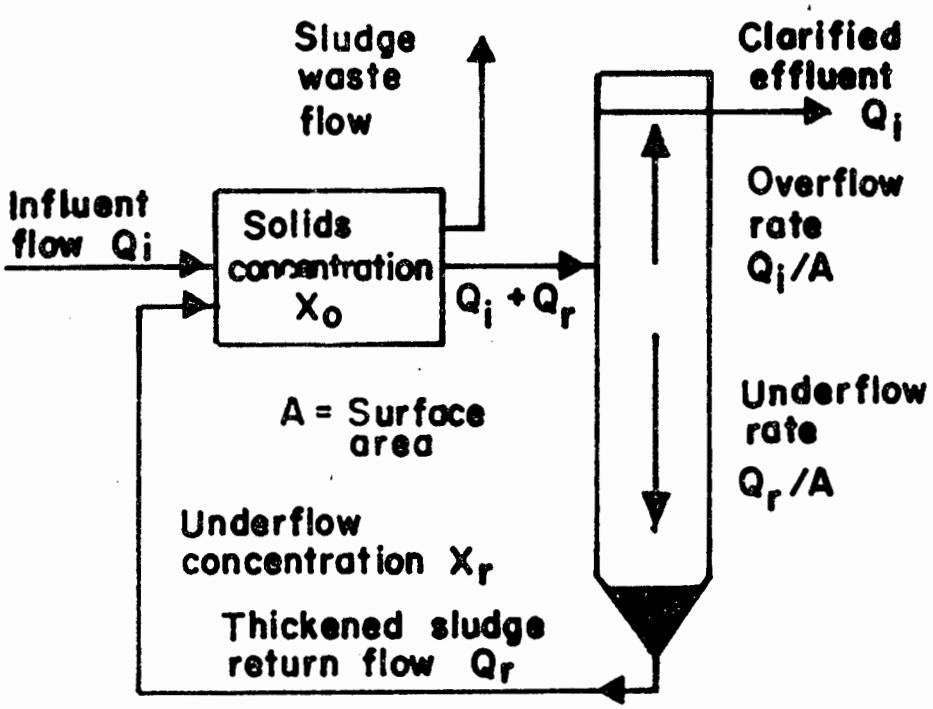

Fig 8.5 Idealized schematic representation of the secondary settling tank in the activated sludge process.

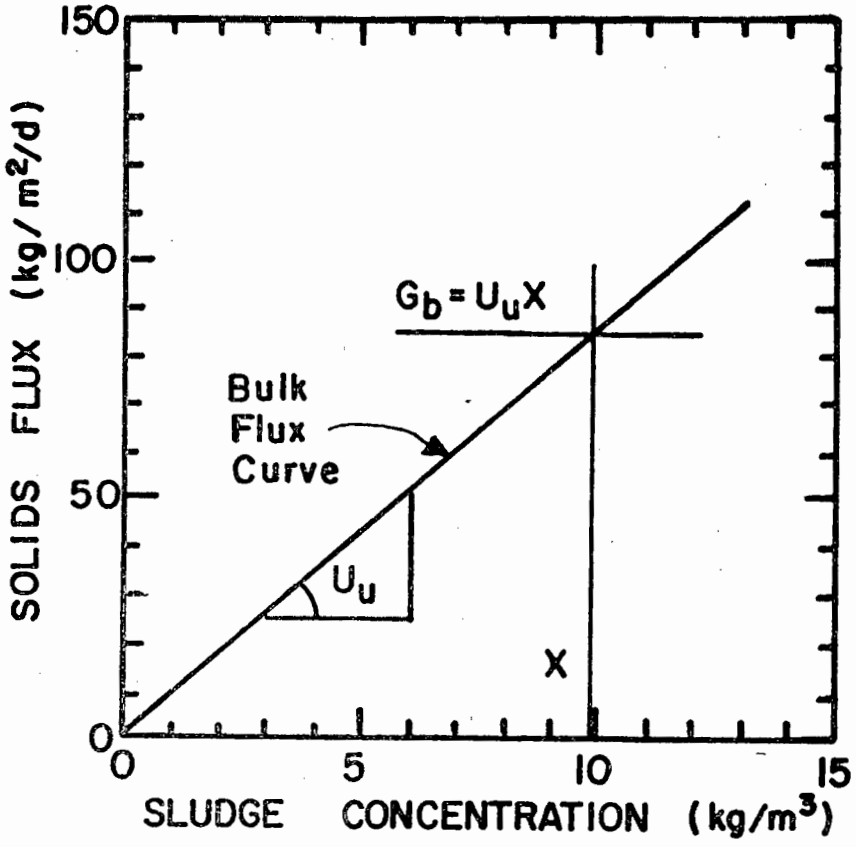

Fig 8.6 The bulk flux curve versus sludge concentration for fixed underflow rate (U_u) i.e. downward sludge transport due to the underflow sludge withdrawal.

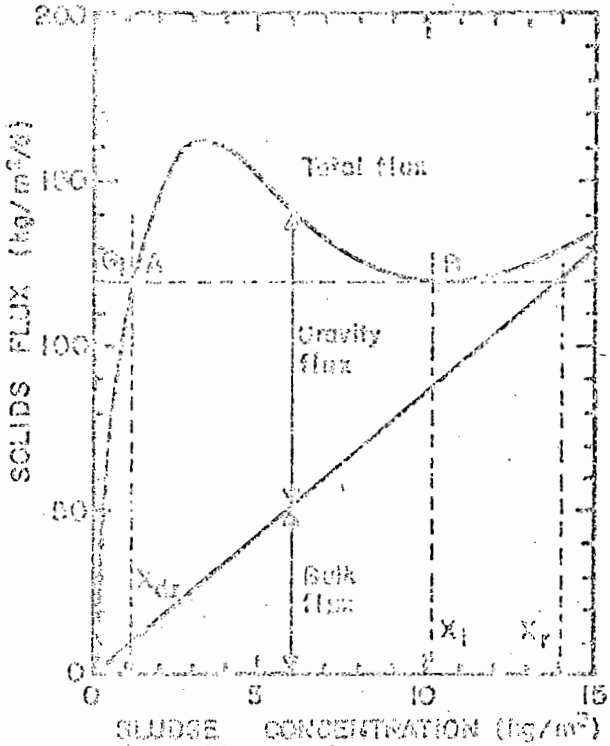

Fig 8.7 Total flux in settling tank versus sludge concentration i.e. downward sludge transport due to gravity sedimentation and underflow sludge withdrawal.

on the settling tank is given by the product of the sludge concentration in the reactor (X_o) and the combined recycle and influent flow ($Q_i + Q_r$) (see Fig. 8.5). Hence, for safe operation of the settling tank

$$G_{ap} \leq G_l \qquad (8.5)$$

where

$$G_{ap} = X_o\ (U_o + U_u) \qquad (8.6)$$

where

X_o = operating MLSS sludge concentration in biological reactor (kg/m³)

U_o = overflow rate

$= Q_i/A$ (see Fig. 8.5) (8.7)

Q_i = influent wastewater flow to process (m³/d)

G_l = limiting flux (kg/m²/d)

From a mass balance around the settling tank, if no sludge is lost over the effluent weirs, the mass of sludge applied is equal to the mass of sludge abstracted via the sludge underflow i.e.

$$Q_r X_r = X_o\ (Q_i + Q_r) \qquad (8.8)$$

where

X_r = MLSS concentration in underflow recycle (kg/m³)

For specified reactor MLSS concentration X_o and influent flow Q_i and selected underflow recycle Q_r, the area A is found by trial and error using the graphical construction shown in Fig. 8.7. The correct value of A is that value which makes Eq (8.5) an equality; values of A which make the LHS > RHS are too small which means settling tank failure in thickening will occur and values of A which make the LHS < RHS are too large which means the settling tank operates successfully but the area can be reduced.

The value of A found by the above procedure is valid only for the specified X_o and Q_i and selected Q_r. By repeating the procedure for different values of Q_r, different values of A will be obtained. For the proposed plant, the maximum area for the anticipated range of Q_r is the required design area.

The clarification criterion is satisfied if the overflow velocity (U_o) is less or equal to the settling velocity of sludge at the concentration at which it is discharged to the settling tank (X_o) i.e.

$$U_o \leqq V_s \text{ at } X_o \qquad (8.9)$$

Clearly the above procedure is extremely tedious because for every choice of Q_r, different total flux curves need to be constructed.

The above graphical design procedure has been considerably streamlined by Yoshioka *et al.* (1957), (see also Dick and Young (1972), Pitman (1980) and White (1975) by introducing the concept of the *state poin* On the gravity flux plot (see Fig. 8.8), the operating sludge concentration (X_o) is represented by a vertical line at the specified X_o value. The overflow rate ($U_o = Q_i/A$) is represented by a line (called the overflow line) from the origin with the slope equal to the overflow rate. The intersection point of the overflow line and the operating concentration line is called the state point. The underflow rate

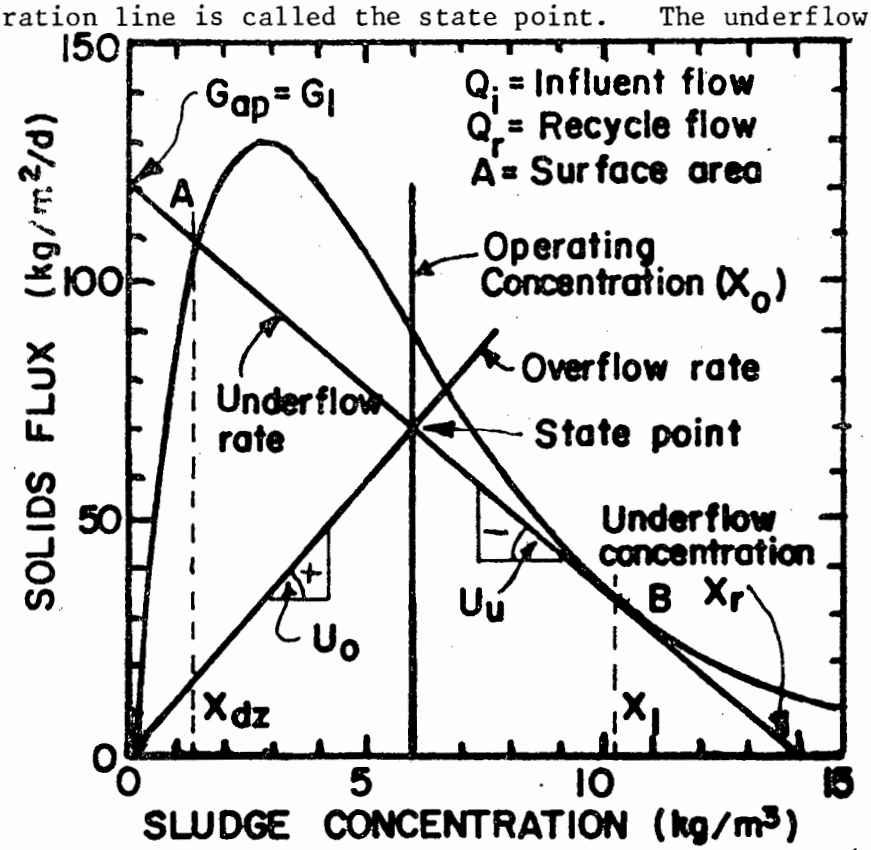

Fig 8.8 The gravity flux curve onto which is superimposed the settling tank behaviour; the state point defines the loading state of the tank and the underflow rate (U_u), overflow rate (U_O) and operating solids concentration (X_O) lines intersect at the state point.

($U_u = Q_r/A$) is represented by a line (called the underflow line) with the slope equal to the underflow rate passing through the state point (see Fig. 8.8). The intersection of the underflow line with the horizontal axis gives the underflow concentration (X_r) (as given by Eq. 8.8) and that with the veritcal axis gives the applied flux G_{ap} (as given by Eq. 8.6).

The state point defines the operating state of the settling tank and operating changes are reflected on the flux curve as follows: (i) a decrease in the underflow rate rotates the underflow line about the state point in an anticlockwise direction while the state point remains in position (see Fig. 8.9a), (ii) an increase in overflow rate rotates the overflow line about the origin in an anticlockwise direction, moves the state point upwards along the operating sludge concentration line while the underflow line slope remains constant but continues to intersect the state point (Fig. 8.9b), (iii) an increase in operating solids concentration moves the operating solids line to the right and because the slopes of the underflow and overflow lines remain unchanged, the state point moves along the overflow line while the underflow line continues to pass through the state point (Fig. 8.9c).

The state of the settling tank, i.e. whether or not it is in an under- or overloaded state, and in the overloaded state, whether failure will occur in its thickening or clarification function, can be obtained from the state point on the gravity flux curve. Referring to Fig. 8.9a, b and c

1) When the state point is within the envelope of the flux curve, the clarification criterion is met and thickening governs the behaviour of the settling tank. When the underflow line

   i) cuts the flux curve at one point only (i.e. near A), safe operating conditions prevail;

   ii) cuts the flux curve at one point only (i.e. near A) and is tangential to the flux curve (i.e. near B), critically loaded conditions prevail;

   iii) cuts the flux curve at 3 points (i.e. once near A and twice near B) overloaded conditions prevail.

2) When the state point is on the flux curve critical conditions with respect to clarification prevail. Under these conditions, thickening will also be critical if the underflow line is tangential to the flux curve on the state point; any underflow rate less than this will cause thickening failure.

3) When the state point is outside the envelope of the flux curve, clarification failure conditions prevail (and thickening also because conditions 1(i) and 1(ii) above cannot be met.

4) When the slope of the underflow line is too steep to make a tangent to the flux curve, but the state point is within the envelope of the flux curve, the thickening criterion no longer needs to be met and clarification only governs the design.

The above conditions can be readily applied to design. For given Q_i and X_o, select A which gives U_o (Eq. 8 .7) and with X_o, fixes the state point. The area A must of course be selected such that the state point falls on or within the flux curve. On the state point, draw the underflow line such that it makes a tangent to the flux curve.

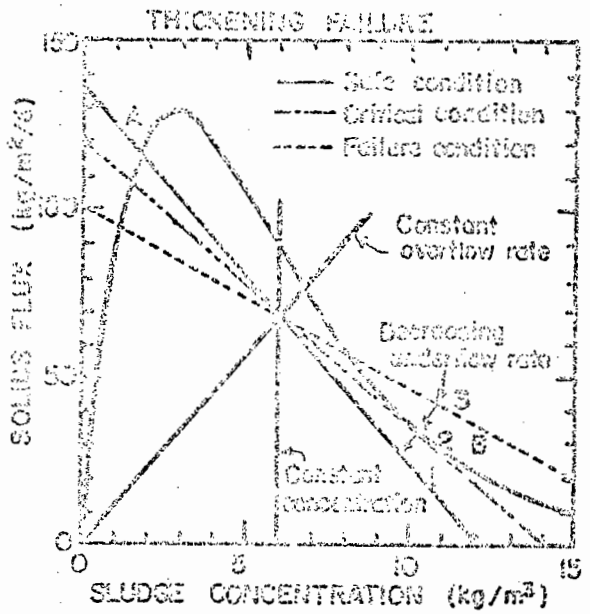

Fig. 8 .9a. Graphical representation of the settling tank operation conditions on the gravity flux curve showing decrease in underflow rate (U_u); (1) safe operating conditions, (2) critically loaded conditions and (3) overloaded conditions.

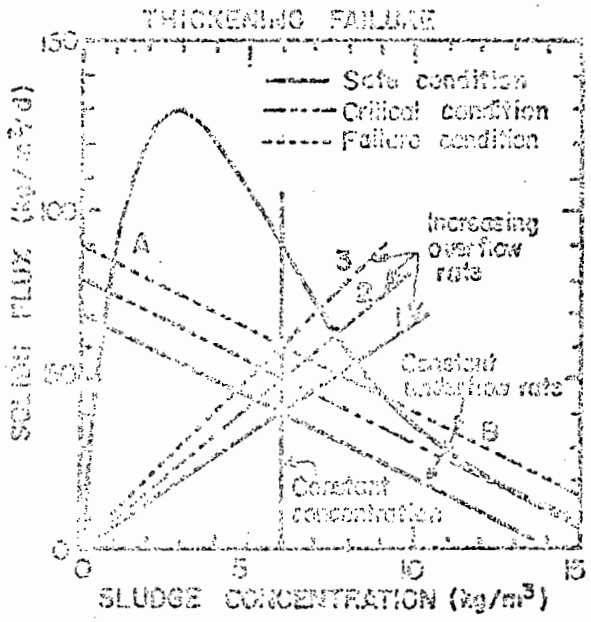

Fig 8 .9b. Graphical representation of the settling tank operation conditions on the gravity flux curve showing increase in overflow rate (U_o); (1) safe operating conditions, (2) critically loaded conditions and (3) overloaded conditions.

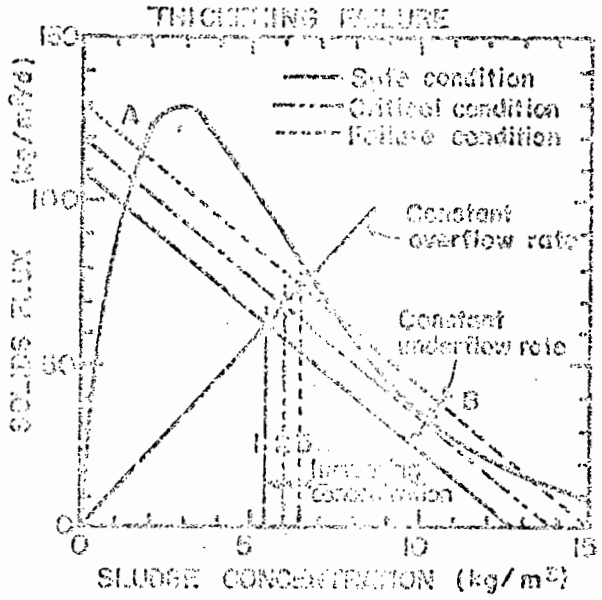

Fig 8.9c. Graphical representation of the settling tank behaviour on the gravity flux curve showing increase in operating solids concentration (X_o); (1) safe operating conditions, (2) critically loaded conditions and (3) overloaded conditions.

From the slope of the underflow line and selected A, determine Q_r (Eq. 8.3). Notice that in this procedure Eqs.(8.5 to 8.9) are being solved graphically: the intercept of the underflow line with the vertical is the applied flux G_{ap} and when the underflow line makes a tangent to the flux curve, the applied flux equals the limiting flux G_1 (see Eq. 8.5 and Fig 8.8).

Although the above procedure is still a trial and error one in that a repeated selection of A is made and the corresponding Q_r for safe operation calculated, it is far simpler than the total flux curve method because each selected A can be analysed on the same flux curve, thus obviating the need for constructing different total flux curves (Fig. 8.7). Note that the two methods give identical results; the condition described by the horizontal line from G_1 in Fig. 8.7 is identical to that described by the underflow line tangential to the flux curve in Fig 8.8.

5.2 Concentration Profiles

The gravity flux curve can also be used to plot idealized sludge concentration profiles in the settling tank (see Alkema, 1971; Pitman, 1978; White, 1975; Vesilind, 1968 and Dick and co-workers, 1967, 1970, 1972). The concentration profiles in the settling tank represented by the safe, critical and overloaded conditions in Figs. 8.9a, b and c are shown in Fig. 8.10. The step changes in concentration shown in Fig. 8.10 are idealized; in practice the changes are more gradual*.

At critically loaded conditions, three concentration zones occur in the settling tank (Fig. 8.10a) (1) the underflow concentration zone in the bottom of concentration X_r where X_r is given by the intercept of the underflow line with the horizontal axis, (ii) the zone settling region where the concentration is equal to the limiting concentration X_1 which causes the limiting flux G_1, where X_1 is given by the concentration at the point of tangency of the underflow line on the flux

*It is the depth required to allow these changes in concentration to take place that governs the design of the depth of the settler. The flux theory *per se* gives only the area requirement for thickening; the depth must be estimated from experience obtained in practice (see Section 7 below) and to allow a certain accumulation of sludge in the settlers (see Section 5.3 below).

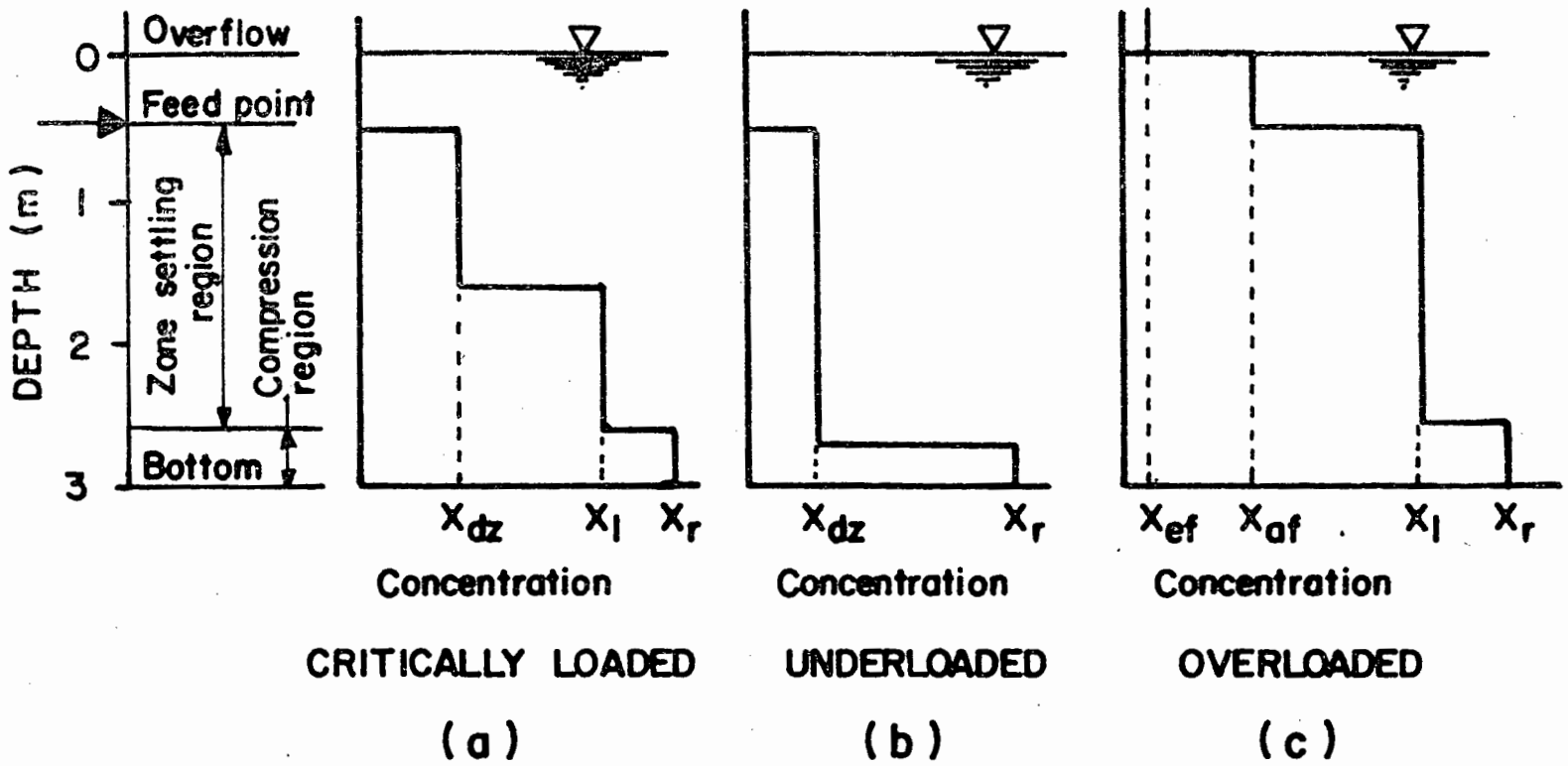

Fig 8.10a *Fig 8.10b* *Fig 8.10c*

Fig 8.10. Sludge concentration versus depth profiles in the settling tank for (i) critically loaded conditions (Fig 8.10a), (ii) underloaded conditions (Fig 8.10b) and overloaded conditions (Fig 8.10c).

curve and (iii) a dilute zone settling region above the zone settling region of concentration X_{dz} where X_{dz} is given by the concentration of the intersection point of the underflow line with the flux curve to the left of the turning point (i.e. near point A on Figs 8.9 a,b and c. Under critically loaded conditions the fluxes of (i) the upper dilute zone, (ii) the zone settling region i.e. the limiting flux G_l and (iii) the underflow withdrawal flux are all equal to the applied flux G_{ap} (Eq 8..6) i.e.

$$G_{ap} = X_o (U_o + U_u) \qquad (8.6)$$

$$= X_{dz} (V_{sxdz} + U_u) \qquad (8.10a)$$

$$= X_l (V_{sxl} + U_u) \qquad (8.10b)$$

$$= X_r U_u \qquad (8.10c)$$

where

V_{sxdz} and V_{sxl} is the settling velocity of the sludge at concentrations X_{dz} and X_l.

The zone settling region of limiting sludge concentration is not stable: the layer will contract or expand depending on whether the conditions are slightly underloaded or overloaded respectively.

When conditions change from a critically loaded to an underloaded condition (by reducing the overflow rate or operating sludge concentration or increasing the underflow rate, see Fig 8.9), the zone settling region will contract downwards until it sinks into the underflow concentration layer. The time taken for the layer to disappear depends on the rate of sludge withdrawal from the tank bottom by the underflow recycle. When steady state conditions again become established, only two concentration zones will be present, (see Fig 8.10b) i.e. the underflow concentration zone X_r and the dilute zone settling region; these concentrations can be found from Eqs 8..10a and c respectively. When conditions change from a critically loaded to an overloaded condition (by increasing the overflow rate or operating sludge concentration or reducing the underflow rate, (see

Fig 8.9), the limiting concentration zone settling region will expand upwards until it reaches the height of the feed point (see Fig 8.10c). The solids transfer to the bottom of the settler is limited by the limiting flux G_l and the difference between the applied flux G_{ap} and G_l is the flux that causes the expansion of the zone settling layer i.e. sludge is being accumulated in the settling tank. The time taken for the zone settling layer to reach the feed point depends on the magnitude of the difference between G_{ap} and G_l, the larger the difference the faster the upward movement. After the zone settling layer reaches the feed point a sludge layer above the feed point develops (see Fig 8.10c). The concentration of this layer is different to the zone settling layer below the feed point because the direction of water flow above the feed point is upwards whereas below the feed point it is downwards (see Fig 8.5). The concentration of the sludge layer above the feed X_{af} can be found from the flux moving upwards, i.e.

$$X_{af} (U_o - V_{sxaf}) = G_{ap} - G_l \qquad (8.11)$$

where

V_{sxaf} = settling velocity of sludge at concentration X_{af}.

When this layer reaches the effluent overflow, sludge loss with the effluent will begin. The concentration that is lost with the effluent X_{ef} given by

$$X_{ef} = (G_{ap} - G_L)/U_o \qquad (8.12)$$

When sludge is lost from the settling tank via the effluent flow, the operating concentration decreases. The operating concentration will continue to decrease until a new critically loaded steady state condition develops (see Fig 8.9c from overloaded to critically loaded conditions). The limiting flux G_l, limiting sludge concentration X_l and underflow concentration X_r which define the sludge handling capacity of the settling tank are given by the vertical axis intercept, tangent point and horizontal axis intercept of the new underflow line tangential to the flux curve and parallel to the existing overload underflow line. Note that this new underflow line does not pass through the existing state point but

but that a new state point will develop at a lower operating concentration (see Fig 8.9c for overloaded to critically loaded conditions).

The above discussion shows that some time elapses between the onset of overloaded conditions and the time of sludge loss with the underflow. The length of time that elapses as well as the concentration of sludge that is lost depend on the severity of the overload (i.e. $G_{ap} - G_1$), the higher the overload, the shorter the time and the higher the concentration.

It should be noted that with overloaded conditions, the concentrations of the sludge profile are not given by the state point condition on the flux diagram. This is because, for the overflow, underflow and sludge operating concentrations lines to intersect at the state point a mass balance between sludge applied and sludge withdrawal by the underflow must be obtained i.e. Eq (8.8) does not apply because sludge will eventually be lost via the overflow. If the overloaded conditions are allowed to persist sludge will be lost from the system thereby reducing the process sludge operating concentration. Consequently, for new stable conditions to develop under a continuous overload, it can be seen that a considerable mass of sludge will be lost to effect the required decrease in operating concentration.

5.3 Dynamic Conditions

Under normal daily operation of the settling tank, the operation sludge concentration and underflow rate can be taken as remaining approximately constant. However the influent flow and hence the overflow changes cyclically over the day (see Fig 8.9b). It may happen that under peak flow conditions, overloaded conditions develop, in which event the zone settling layer will begin to rise. The overload, depending on its severity, may persist for a few hours without any sludge loss, by which time the peak flow period may have passed and the zone settling layer again begins to drop. Consequently, over the day, the sludge layer will move up and down and and the settler may even experience a temporary overload without sludge loss in the effluent (Tracy and Keinath, 1973).

The principal factor that prevents sludge loss during a temporary overload is sludge storage, which, once the area has been designed appropriately according to the flux theory, is directly proportional to the depth of the settler. Generally the deeper the settler, the greater the temporary overload that can be sustained without sludge loss. Unfortunately, no guidance regarding the design of the depth can be derived from the flux theory *per se* and the depth is best based on practical experience. A depth of 3 to 4 m appears to be adequate (see Section 7 below). Deep tanks also have the advantage that allowance is made for the various concentration zones such as the underflow concentration zone where sludge compression occurs. Under cyclic loading conditions the compression zone depth also varies in accordance with the load, being deeper at the peak flow period. Deep tanks are also less prone to disturbance of the settling zone sludge layers caused by hydraulic turbulence of the discharge and sludge withdrawal flows (see also Section 6.5 below).

5.4 Discussion

Clearly the graphical approach to the flux theory described above gives considerable insight into the design and operation of secondary settlers taking due consideration of the settling characteristics of the sludge. However, despite convenient developments in the graphical approach, the procedure remains rather tedious as for each sludge concentration, the settling velocity versus sludge concentration curve needs to be consulted to estimate the settling velocity. Perhaps the biggest drawback is that the differences between the settling characteristics of different sludges can only be described graphically.

6. ANALYTICAL APPLICATION OF FLUX THEORY

6.1 Empirical Equation for Settling Velocity versus Sludge Concentration

In order to overcome the difficulties associated with the graphical approach, research has been undertaken to find an empirical relationship between the settling velocity and sludge concentration. Such a relationship would allow direct analytical

solutions to the design equations.

Many mathematical expressions linking the settling velocity and sludge concentration have been proposed but the two most widely accepted are the following

$$V_s = V_o X^{-n} \quad (8.13)$$

$$V_s = V_o e^{-nX} \quad (8.14)$$

where

V_s = settling velocity (m/d)

X = MLSS concentration (kg/m³)

V_o, n = constants describing settling characteristics of sludge.

The first expression can be represented by a straight line on a log V_s versus logX plot (i.e. log - log), the second by a straight line on a log V_s versus natural X plot (i.e. semi-log). Considerable research effort has been expended to establish the applicability of each expression to flux theory - Dick and Young, 1972 and Pitman, 1978 using Eq(8.13) and Vesilind, 1968a, 1968b and White, 1975 using Eq (8.14). A comprehensive comparison is presented by Smollen (1981), who concluded that Eq (8.14) is superior to Eq (8.13) because it (1) gives a theoretically consistent description of the observed gravity flux curve with defined turning and inflexion points and (2) gives a closer correlation with data measured on laboratory, pilot and full scale plants over a number of years ($r^2 > 0,95$). Consequently in this chapter, Eq (8.14) is accepted for describing the interface zone settling velocity versus sludge concentration in the batch settling test.

The settling characteristics V_o and n are readily obtained by linear least squares regression analysis of multiple batch test settling data over a range of sludge concentrations from 1,5 kg/m³ to 15 kg/m³ on the expression (see Fig 8.11)

$$\log V_s = V_o - nX/2,303 \quad (8.15)$$

Substituting Eq (8.14) for V_s into Eq (8.1) yields the gravity flux in terms of the concentration and settling characteristics i.e.

$$G_s = X V_o e^{-nX} \qquad (8.16)$$

Equation (8.16) describes the gravity flux curve shown in Fig 8.4.

6.2 Mathematical Properties of Theoretical Flux Equation

The slope of the flux curve is given by the derivative of Eq (8.16) i.e.

$$dG_s/dX = V_o e^{-nX}(1 - nX) \qquad (8.17)$$

which, when set to zero, gives a turning point at X = +1/n and a maximum flux of V_o/ne. Differentiating Eq (8.17) with respect to X and substituting 1/n for X shows that the turning point with co-ordinates ($X = 1/n$; $G = V_o/ne$) is a maximum. Setting the second derivative to zero shows that there is an inflexion point in the flux curve at co-ordinates ($X = 2/n$; $G = 2V_o/ne^2$).

From an inspection of the flux curve, no tangential underflow line can be constructed on the flux curve (see Section 5.1 above) with a slope greater than that of the flux curve at the inflexion point. The intercepts of the tangent at the inflexion point with the vertical and horizontal axes therefore give respectively the maximum limiting flux (G_{lmax}) minimum underflow concentration (X_{rmin}) for thickening to govern the design of the settling tank. The slope of this tangent is $-V_o/e^2$ (from Eq 8.17), and hence

$$G_{lmax} = 4V_o/ne^2 = 2.G_{IP} = 2/e.G_{max} \qquad (8.18)$$

$$X_{rmin} = 4/n \quad = 2.X_{IP} = 4.X_{TP} \qquad (8.19)$$

where subscripts IP and TP refer respectively to the inflexion and turning points.

The above features of the flux curve are shown in Fig 12.12.

6.3 Application of Flux Equation to Settling Tanks

Defining s as the underflow recycle ratio, i.e.

$$s = Q_r/Q_i \qquad (8.20)$$

the maximum overflow rate to satisfy the thickening criterion is found from Eqs (8.3 and 8.5 to 8.8) and is given by

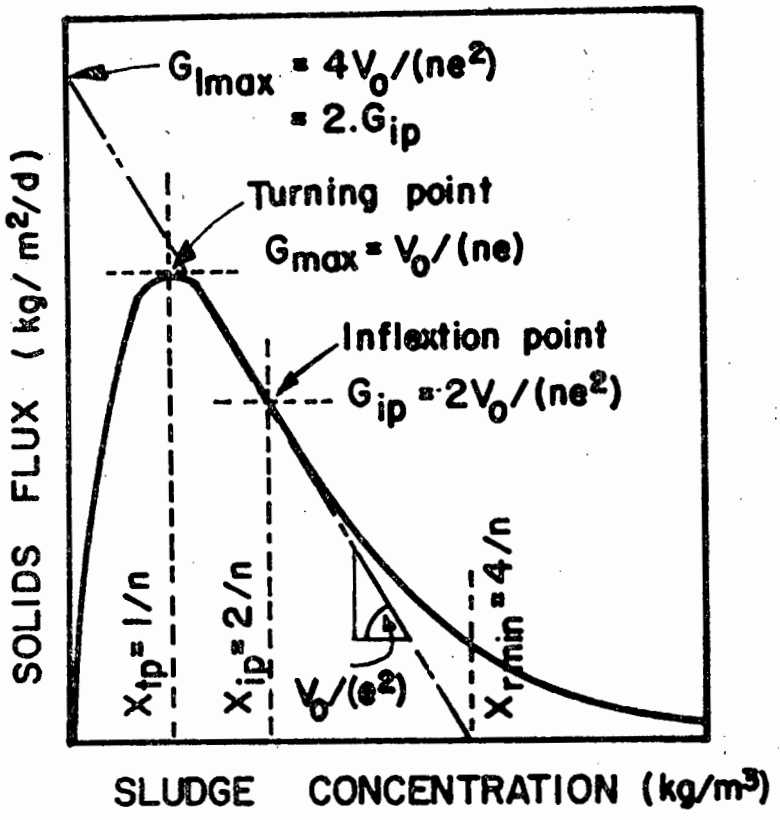

Fig 8.12 Mathematical properties of the flux curve based on the settling velocity-sludge concentration equation $V_s = V_o \exp(-nX)$.

$$Q_i/A = G_1/\{X_o(1 + s)\} = G_1/(X_r s) \qquad (8.21)$$

where

$$X_r = (1 + s)X_o/s \qquad (8.22)$$

The equation of the underflow line with a point of tangency to the flux curve is

$$G = G_1(1 - X/X_r) \qquad (8.23)$$

and its slope is

$$dG/dX = -G_1/X_r \qquad (8.24)$$

At the point of tangency (see Fig 8.8) $X = X_1$, and both the fluxes and the slopes of the flux curve and the underflow tangent are equal i.e. Eq (8.16) = Eq (8.23) and Eq(8.17) = Eq(8.24). From these equations taking X_r as known, solving for X_1 and, ignoring the impractical solution, yields

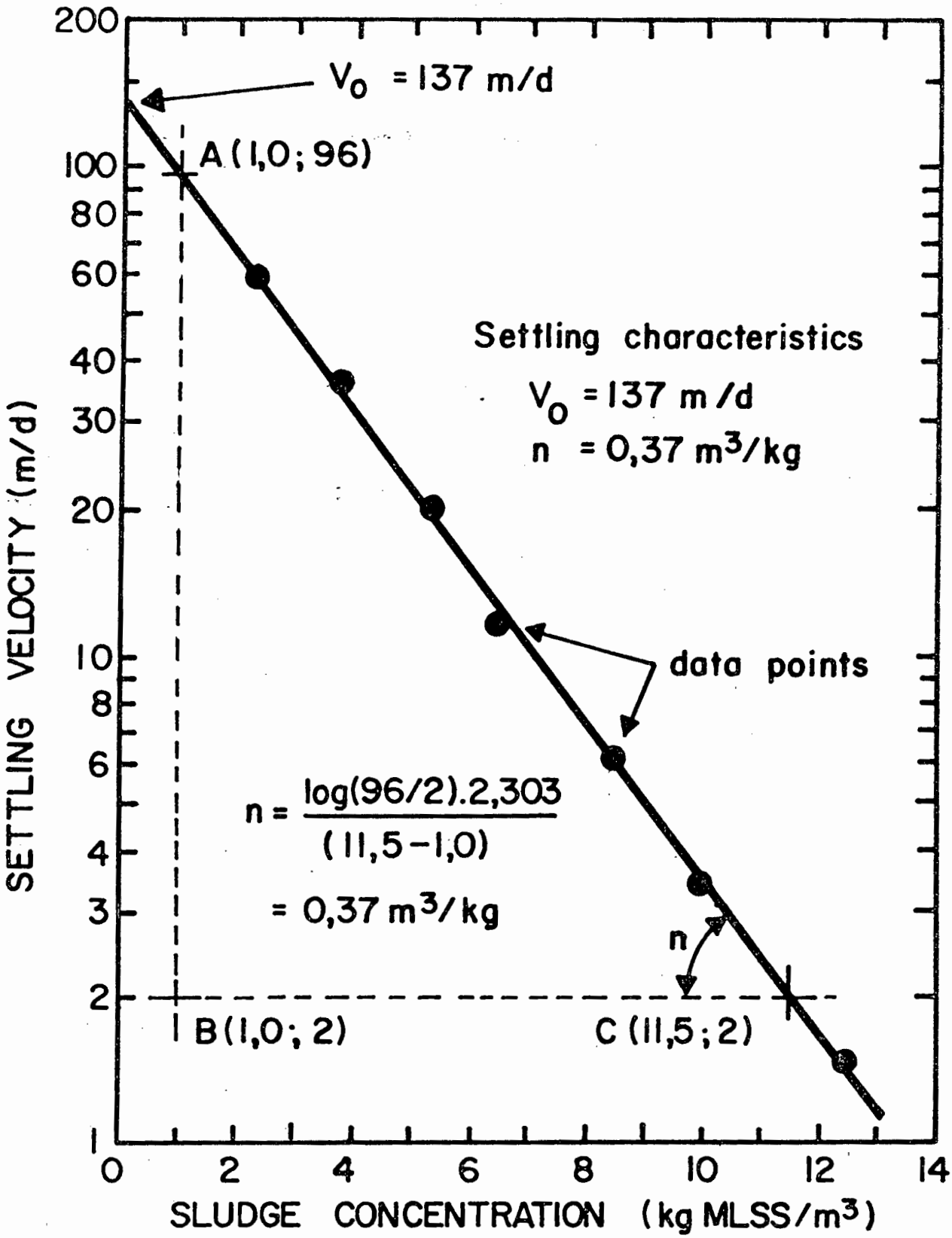

Fig 8.11 Determination of settling characteristics V_o and n from multiple batch test settling data.

$$X_l = (X_r/2)\{1 + \sqrt{1 - 4/(nX_r)}\} \qquad (8.25)$$

Substituting Eq (8.25) into Eq (8.16) gives the limiting flux i.e.

$$G_l = V_o X_r \frac{(1+\alpha)}{1-\alpha)} \exp\{-nX_r(1+\alpha)/2\} \qquad (8.26a)$$

where

$$\alpha = \sqrt{1 - 4/(nX_r)} \qquad (8.26b)$$

If $\alpha < 0$, there is no solution for G_l. Setting $\alpha = 0$ yields $X_r = 4/n$ and hence $G_l = 4V_o/ne^2$ which corresponds to X_{rmin} and G_{lmax} respectively as found above (see Fig 8.11). No solution for G_l is possible for $X_r < 4/n$ because the curvature of the flux curve is such that no valid tangential underflow line can be constructed within the envelope of the flux curve. This result can be interpreted as the thickening criterion not being important in a design when $X_r < 4/n$, leaving only the clarification criterion to be met (see condition 4 in Section 5.1 above).

Substituting Eq (8.22) for X_r into Eq (8.26) and substituting Eq (8.26) into Eq (8.21) yields

$$\frac{Q_i}{A} = \frac{V_o}{s} \frac{(1+\alpha)}{(1-\alpha)} \exp\{-n(1+s)X_o(1+\alpha)/(2s)\} \qquad (8.27a)$$

where

$$\alpha = \sqrt{1-4s/\{n(1+s)X_o\}} \qquad (8.27b)$$

Equation (8.27) relates the overflow rate to the recycle ratio, s, for a selected value of the sludge concentration in the reactor and settling characteristics of the sludge to meet the thickening criterion. If $\alpha = 0$, $X_o = 4s/(1+s)n$. Hence from Eq (8.27), if $\alpha = 0$

$$\frac{Q_i}{A} = V_o/(e^2 s) \qquad (8.28)$$

Consequently, if Q_i/A is less than $V_o/(e^2 s)$ then both the thickening and clarification criteria have to be met. If Q_i/A is greater than $V_o/(e^2 s)$, then thickening apparently is not a governing criterion and the clarification criterion only has to be met. This

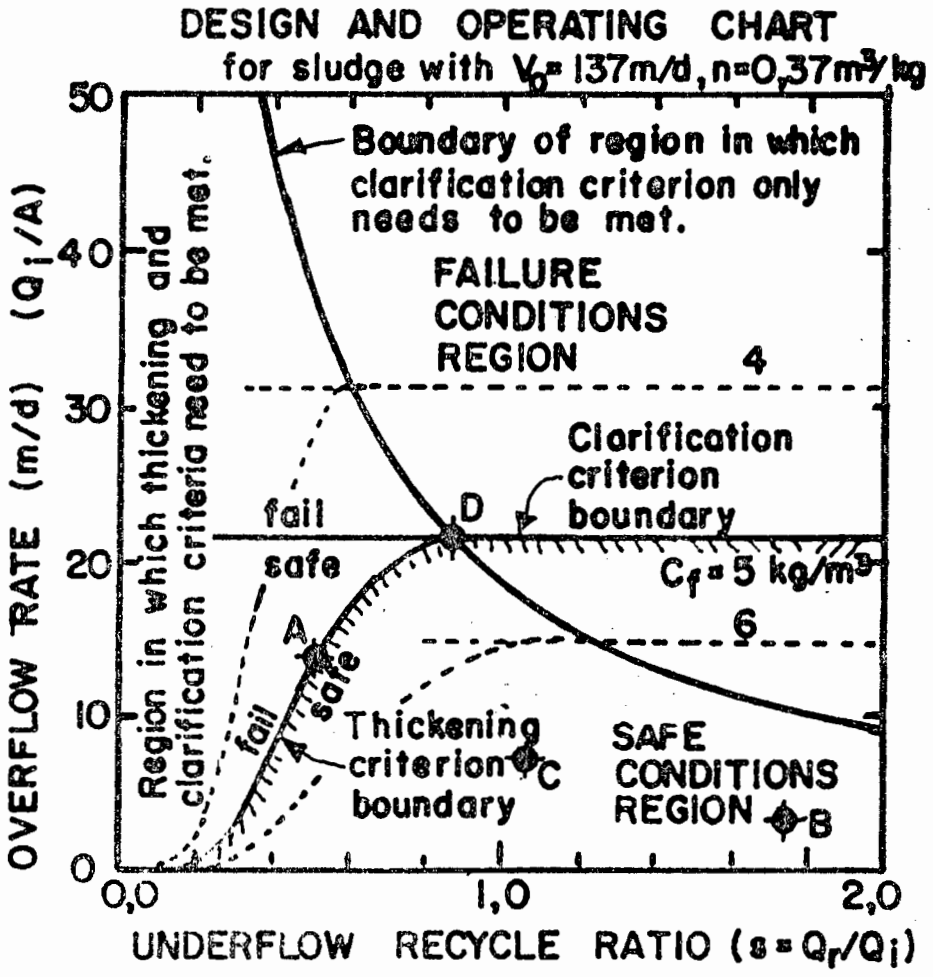

Fig 8.13 Design and operating chart for secondary settlings showing the different type of failure that can occur for different combinations of overflow rate and underflow recycle ratio.

criterion is met if the overflow rate is less than the settling velocity of the sludge at the feed concentration i.e. from Eq (8.9)

$$Q_i/A = V_o e^{-nX_o} \qquad (8.29)$$

6.4 Settling Tank Design and Operating Chart

By plotting Q_i/A versus s from Eqs (8.27 to 8.29) for different values of X_o, a steady state design and operating chart for the settling tank is obtained (Fig 8.13). The hyperbola on the diagram described by Eq (8.28) distinguishes between the domain in which both the thickening and clarification criteria have to be met (area between axes and hyperbola) and in which the clarification only has to be met (area above hyperbola). The thickening criterion is given by Eq (8.27) which, for different X_o values, is a family of curves from the hyperbola to the origin. These curves show that as underflow recycle ratio s decreases the allowable overflow rate decreases. The clarification criterion is given by Eq (8.29) and being independent of s, is a family of horizontal lines. In the region below the hyperbola, the thickening and clarification criteria have to be met simultaneously. In some instances in this region, the allowable overflow rate is higher for thickening than for clarification so that clarification is the governing criterion for the settling tank. Consequently for a specified reactor concentration X_o, *failure* of the settling tank is represented by overflow rate-underflow recycle ratio data pairs falling above the thickening and the clarification lines.

It should be noted that the design and operation chart is also valid for daily cyclic conditions. For successful operation of the settling tank, the conditions prescribed by the design and operation chart need to be met at any instant of the day. For example, for a fixed settling tank area (A) and underflow rate (Q_r), as the influent flow to the plant (Q_i) increases, so the overflow rate (Q_i/A) increases and the recycle ratio (s) decreases, which moves the intersection point of the overflow rate and recycle ratio upwards to the left in Fig 8.13. At each instant of the day, the overflow rate and recycle ratio intersection point must subscribe

to the thickening and clarification criterion in the diagram i.e. must at all times be below the thickening and clarification lines.

6.5 Design Example

Assume that the MLSS concentration of the nutrient removal processes designed in Chapters 4, 5, 6 and 7 is 5 kg/m³. For the nutrient removal process, the settling characteristics are selected to be rather poor i.e. V_o = 137 m/d or 5,7 m/h and n = 0,37 m³/kg giving V_o/n = 15,4 kg/m²/h (see Table 12.1). The average dry weather flow (ADWF) is 13,3 Mℓ/d and assume that over the day the flow varies in a cyclic pattern with a minimum (MDWF) of 0,6.ADWF and a peak (PDWF) of 2,0 ADWF, and the peak wet weather flow (PWWF) is estimated to be 3,0.ADWF.

For the settling characteristics of the sludge the design and operating chart is constructed as set out above (see Fig 8 .13). Assume that at PWWF, clarification must be achieved and that the thickening criterion will be met by adjusting the underflow recycle. The PWWF is 3.13,3 = 40 Ml/d. From Fig 8..13 the maximum overflow rate at X_o = 5 kg/m³ is 21 m/d (given by horizontal clarification criterion line). Hence the settling tank area is $40.10^3/21$ = 1905 m². In order that thickening failure does not occur under PWWF conditions, the recycle ratio at PWWF must be greater than 0,82 (given by the s value of the intersection point of the clarification line and the hyperbola, see point D on Fig 8.13). Hence at PWWF of 40 Ml/d the underflow Q_r should be 0,82.40 = 32,8 Ml/d or 2,46 times ADWF otherwise thickening failure will occur (i.e. for s < 0,82, the Q_i/A and s intersection point will fall above the thickening criterion line in Fig 8!.13).

Under dry weather conditions, the overflow rate at PDWF is $2,0.13,3.10^3/1905$ = 14 m/d. In order that thickening failure does not take place at PDWF, the underflow recycle ratio s must be at least 0,52 (given by the s value of the intersection point of the horizontal Q_i/A = 14 m/d line and the thickening criterion line for X_o = 5 kg/m³ see point A on Fig 8.13). Hence the underflow should be at least 0,52.26,6 = 13,9 Mℓ/d or approximately 1:1 based on ADWF. Accepting the settling tank area of 1905 m² and fixing the recycle flow at a constant 14 Mℓ/d,

the overflow rate and recycle ratio at ADWF are 7 m/d and 1,05:1, at MDWF are 4,2 m/d and 1,75:1 and at PWWF are 14 m/d and 0,52 respectively. Hence in the design and operating chart, the locus of the points defining the operating conditions over the day under cyclic influent flow moves between points of co-ordinates Q_i/A = 14 m/d and s = 0,52 at PDWF (see point A in Fig 8.13) and Q_i/A = 4,2 m/d and s = 1,75 at MDWF (see point B in Fig 8.13) through Q_i/A = 7,0 m/d and s = 1,05 at ADWF (see point C in Fig 8.13). From the chart, all these points represent safe operating conditions with respect to thickening and clarification and hence under dry weather conditions, the settling tank should operate satisfactorily. Provision for wet weather flow was made up to a PWWF of 3.ADWF but the underflow recycle needs to be increased to 32,8 Ml/d to accommodate this. For lower PWWF, the underflow need not be increased so high. The required underflow can be determined from the design and operating chart.

The above design is based on the accepted settling characteristics V_o = 137 m/d and n = 0,37 m^3/kg and should the actual characteristics be better than these the settling tanks will still operate satisfactorily. However, if the settling characteristics are poorer than the accepted ones, difficulty in operating the settling tank may be encountered. To a degree, a deterioration in settling characteristics can be accommodated under dry weather conditions by increasing the underflow recycle but this strategy depends on how poor the characteristics are below the accepted ones; however to increase the underflow recycle beyond the value where the thickening criterion no longer needs to be met will not improve the situation and will be wasted on pumping costs. Under peak wet weather conditions, sludge will probably be lost depending on the duration of the peak wet weather flow.

High peak wet weather flows can be accommodated by the settling tank by allowing them to bypass the main biological process and discharging them to the effluent from the last aerobic reactor. Although the overflow rate in the settling tank still increases, the applied flux to the settling tank does not increase due to the dilution of the mixed liquor concentration by the influent. The effect of this is to discharge to the settling tank a significantly

reduced operating sludge concentration. In contrast, if the storm flow is discharged to the head of the biological process, both the overflow rate and applied flux would increase and a large mass of sludge would be displaced from the biological process to the settling tank. The emergency strategy of bypassing storm flows is permissible because usually storm flows are very low in COD, TKN and P concentrations and a short contact period with the mixed liquor in the settling tank will significantly reduce the COD and TKN; however a higher P concentration may have to be accepted for the short duration of the storm flow.

7. PRACTICAL ASPECTS OF FINAL CLARIFIER DESIGN

The basic purposes of activated sludge final clarifiers are to produce a clear effluent free of suspended solids and a thickened sludge for recycle to the inlet of the process. However, in nutrient removal versions, two additional requirements are desired. The quality of the underflow sludge should be such that a large mass of nitrate is not recycled to the anaerobic zone. Also, if the anaerobic conditioning of the activated sludge can be initiated in the bottom of the clarifier it will benefit phosphate removal.

Full-scale experience on sloping bottom scraped clarifiers has shown that the solids in the sludge layer move in semi-plug flow and despite their endogenous nature, can denitrify quite well. For example, up to 5 mgN/ℓ nitrate can be lost on passing through this layer and if denitrification is complete, anaerobic conditions are initiated. The phosphate released under these anaerobic conditions will not cause problems as it is usually trapped in the sludge layer and moves out with the return sludge before diffusing into the effluent.

If the sludge can be encouraged to thicken well in the clarifier, denitrification will be favoured even more. For example, if the sludge is thickened up to give a recycle concentration of 20 000 mg/ℓ instead of 10 000 mg/ℓ, half the mass of nitrate will be returned even if no denitrification occurred at all. However, at 20 000 mg/ℓ solids the ratio of biomass to nitrate is very large and despite the endogenous nature of the bacteria present, very good

denitrification will occur in most cases using up all the available nitrate. Under this situation there will be no nitrate feedback to the anaerobic zone. Of course, the ability to thicken up to 10 000 mg/ℓ solids will depend on the sludge properties and will usually only happen with low SVI sludges (i.e. less than 100 mℓ/g). In this respect operators should be encouraged to ensure that such sludges are produced in this process.

The denitrification and anaerobic conditions that can be encouraged in final clarifiers can only be of benefit to the process and designers should bear this in mind in clarifier design.

As mentioned earlier, good denitrification has been noticed on full-scale sloping bottom scraped clarifiers as well as in conical bottom (60° cone) settling tanks. However, these effects are less pronounced on flat-bottomed suction scraped clarifiers, as these are designed to lift settled sludge off the floor before it has the opportunity to denitrify. It has also been found that suction type clarifiers tend to return a relatively weak sludge and if attempts are made to thicken the sludge and so obtain better denitrification, the sludge will refuse to pass up the withdrawal tubes due to its increased viscosity. Also, the rotating suction arm tends to cause hydraulic instability in the tank at high recycle rates.

Therefore with the view to encouraging denitrification in final clarifiers and the initiation of anaerobic conditions in the return sludge, these clarifiers should incorporate the following features:

(i) they should preferably be circular and a sloping bottom with mechanised scrapers to move sludge to a contral bottom withdrawal point,

(ii) mixed liquor to be introduced near the surface at the centre with the inlet system being well baffled to destroy kinetic energy of the influent,

(iii) the side water depth should be at least 4 m,

(iv) the sludge withdrawal system should be designed to handle sludges with a higher viscosity than water.

The clarifier surface area has a very important influence on performance. It is recommended that the solids flux theory (described in Sections 5 and 6 above) be used to determine this. The Vesilind equation:

$$V = V_o e^{-nx}$$

which describes the settling of activated sludge is an important aspect of this theory with the two factors V_o and n varying with sludge settling properties. Experimentally derived values of these factors can show a large variation depending on the degree of filamentous growths in the sludge.

Typical results obtained are shown in Table 8.1 in order of deteriorating settling properties.

Table 8.1 Settling characteristics observed at four different activated sludge plants in Johannesburg.

Plant	V_o (m/h)*	n (m^3/kg)	V_o/n (kg/m^2/h)*	SVI (mℓ/g)
A. NORTHERN WORKS MODULE 2				
mean value	7,90	0,29	27,24	100
best result	9,49	0,28	35,89	65
worst result	6,07	0,35	17,34	180
B. NORTHERN WORKS MODULE 1				
mean value	7,94	0,36	22,06	120
best result	9,49	0,27	35,16	70
worst result	7,02	0,40	17,55	170
C. GOUDKOPPIES MODULE 2				
mean value	6,68	0,40	16,70	210
best result	9,84	0,31	31,7	70
worst result	3,84	0,37	10,4	300
D. GOUDKOPPIES MODULE 1				
mean value	5,95	0,43	13,8	250
best result	8,96	0,41	21,9	130
worst result	5,20	0,55	9,5	300

It was found that the ratio V_o/n is a very good indicator of settling properties which correlates with more wellknown parameters such as SVI. Thus, it can be seen in Table 8.1 that Plant D has a poor settling sludge; the sludge in Plant A settles fairly well. High values of this ratio (i.e. 30 kg/m^2/h)

*To convert to units per day, multiply by 24.

indicate good settling properties, while low values (i.e. 10 kg/m²/h) are found with poor settling sludges. Designers must decide what types of sludges are likely to occur in their plant during its life-time. If they are sure that poor settling sludges will never be encountered, a V_o/n ratio of 30 or above can be used but if poor settling sludgs are encountered, values of less than 15 must be chosen. However, this decision must be taken carefully as a value of 15 will lead to a clarifier design with twice the surface area than would be obtained using $V_o/n = 30$. It should also be noted that experience to date has shown that biological nutrient removal plants can be prone to the encouragement of filamentous growths which give rise to poor settling sludges so that a conservative approach to clarifier design might be prudent.

Plant operation can also have a dramatic effect on activated sludge settling properties and hence V_o/n values. An important variable is the dissolved oxygen concentration in aerobic zones. It has been found both in South Africa and overseas that plants run at low dissolved oxygen concentrations (below 1,0 mg/ℓ and in particular, below 0,5 mg/ℓ) are prone to the growth of filamentous bacteria which are the cause of poor settling sludges. Designers should therefore bear in mind the quality of operation that will be available, in particular, skills for the control of dissolved oxygen input and process overloads.

Another factor to be remembered is that the solids-flux theory covered in this chapter assumes an idealised settling tank which will not occur in practice and although it has been found that some full-scale clarifiers obey the flux model within 20%, designers should make use of safety factors either in the initial choice of V_o and n or applied to the final clarifier area claculated from this model.

8. REFERENCES

1. Alkema K L (1971) The effect of settler dynamics on the activated sludge process. M Sc thesis, Dept. of Chemical Engineering, Univ. of Colorado.

2. Bratby J R and G v R Marais (1976) A guide for the design of dissolved-air (pressure) flotation systems for activated sludge processes. Water SA, 2, 2, 87-100.

3. Bratby J R and G v R Marais (1977) Aspects of sludge thickening by dissolved-air flotation, Wat.Pollut.Control, 77, 3, 421-432.

4. Coe H S and G H Clevenger (1916) Methods for determining the capacities of slime settling tanks, Trans.Am.Inst. Mining Eng., 55, 356.

5. Dick R I (1967) Evaluation of activated sludge thickening theories, J.Sanit.Eng.Div., ASCE, 93, SA4.

6. Dick R I (1970) Role of activated sludge final settling tanks, J.Sanit.Eng.Div., ASCE, 96, 423.

7. Dick R I and K W Young (1972) Analysis of thickening performance of final settling tanks, Prod. 27th Ind.Waste Conf., Purdue Univ., Series No. 161, Lafayette, Indiana.

8. Kynch G J (1952) A theory of sedimentation, Trans.Faraday Soc., 48, 166.

9. Pitman A R (1980) Settling properties of extended aeration sludges, JWFCF, 52, 3.

10. Smollen M (1981) Behaviour of secondary settling tanks in activated sludge processes, M Sc thesis, Dept. of Civil Eng., Univ. of Cape Town.

11. Tracy K D and T M Keinath (1973) Dynamic model for thickening of activated sludge, Water 1973, 70, 136, Chem. Eng. Progress, Symp.Series AIChE.

12. Vesilind P A (1968a) Design of prototype thickeners from batch settling tests, Wat. and Sew. Works, 115, 302.

13. Vesilind P A (1968b) Discussion of evaluation of activated sludge thickening theories, J.Sanit.Eng.Div., ASCE, 94, SA1, 185-190.

14. White M J D (1975) Settling of activated sludge. Tech.Rep. TR11, Water Research Centre, Medenham, England.

15. Yoshioka N, Y Hotta, S Tanaka, S Naito and S Tsugami (1957). Continuous thickening of homogenous flocculated suspensions, Chem.Eng., Tokyo, 21, 66.

APPENDIX 1

LIST OF SYMBOLS

a	=	mixed liquor recycle ratio from the aerobic to the anoxic reactors.
a_o		Subscript o denotes optimum.
A	=	surface area of secondary settling tank
b_{hT}	=	endogenous mass loss rate for heterotrophic organisms at T°C)/d)
	=	$b_{h20}(1,029)^{(T-20)}$
b_{nT}	=	endogenous respiration rate for nitrifying bacteria at T°C (/d)
	=	$b_{n20}(1,029)^{(T-20)}$
b_{h20}	=	the rate at 20°C = 0,24/d
b_{n20}	=	the rate at 20°C = 0,04/d
D_p	=	denitrification potential (mgN/ℓ influent)
D_{p1}, D_{p3}		Subscripts 1 and 3 refer respectively to the primary and secondary anoxic reactors
D_{pd1}, D_{pd2}		Subscripts d1 and d2 refer respectively to the first and second anoxic reactor of a Modified UCT process
D_{pp}	=	denitrification potential of the process when the maximum anoxic sludge mass fraction is all in the form of a primary anoxic reactor
f	=	unbiodegradable fraction of active mass = 0,20 mgVSS/mgVSS
f_{av}, f_{at}	=	active fraction of the sludge mass with respect to the volatile and total solids concentrations respectively
f_{bs}	=	readily biodegradable COD fraction of the influent with respect to the biodegradable COD concentration
f_{cv}	=	COD to VSS ratio of the volatile sludge mass = 1,48 mgCOD/mgVSS
f_i	=	MLVSS to MLSS concentration ratio of the mixed liquor
f_n	=	nitrogen fraction of the MLVSS (mgN/mgVSS) = 0,10 mgN/mgVSS
f_{na}	=	ammonia fraction of the influent TKN
f_{nu}	=	soluble unbiodegradable organic nitrogen fraction of the influent TKN

f_{ns} = TKN/COD concentration ratio of the influent

f_p = phosphorus fraction of the inert MLVSS and endogenous residue MLVSS = 0,015 mgP/mgVSS

f_{rps} = fraction of raw total COD removed by primary sedimentation

f_u = unbiodegradable COD fractions in the influent (mgCOD/mgCOD). Additional subscripts p and s refer respectively to particulate and soluble fractions

f_{up}, f_{us}

f_v^* = general parameter for volume fractions

f_x^* = general parameter for sludge mass fractions

*Additional subscripts a, b, d, 1, 3 and m refer respectively to anaerobic, total aerobic, total anoxic, primary anoxic, secondary anoxic and maximum unaerated allowable

f_{xdt}, f_{xdm} Additional subscripts 5 and m following the d subscript refer respectively to the total and maximum allowable sludge mass fractions

f_{x1min}, f_{x3min} Subscript min following subscripts 1 and 3 refer to the minimum primary and secondary anoxic sludge mass fractions

f_{xd1}, f_{xd2} Subscripts 1 and 2 following the d subscript refers respectively to the first and second anoxic reactors of a Modified UCT process

F/M = Food to Microorganism ratio

G = General parameter denoting flux ($kg/m^3/d$) Subscripts ap, b, 1 and s refer respectively to applied flux, bulk flux, limiting flux and gravity settling flux

K, K_1, K_2, K_3 = general parameter for denitrification rate ($mgNO_3$/mgVASS/d). Subscripts 1 and 2 refer respectively to the 1st and 2nd rates in the primary anoxic and 3 to the rate in the secondary anoxic. Additional subscripts T and 20 refer to T°C and 20°C respectively

K_r = conversion rate of biodegradable organic nitrogen to free and saline ammonia by active mass = 0,018ℓ/mgVASS/d. Subscript T and 20 refer to rates at 5°C and 20°C

K_n = half saturation coefficient in Monod equation for nitrification = 1 mgN/ℓ.

Subscripts T and 20 refer respectively to T°C and 20°C.

Subscripts pH and 7,2 refer respectively to K_n at different pH values and that at pH 7,2

LF = load factor

M	=	prefix denoting mass as opposed to concentration of a variable
N	=	general parameter denoting nitrogen concentration (mgN/ℓ)
N_a N_n N_o N_t N_u	=	Subscripts a, n, o, t and u refer respectively to ammonia, nitrate, biodegradable organic nitrogen, total TKN and soluble unbiodegradable organic nitrogen concentrations. Additional subscripts e, i, r, s and a refer respectively to the concentrations in the effluent, influent, r-, s- and a-recycle flows
N_c	=	nitrification capacity (mgN/ℓ influent)
N_{pi}	=	unbiodegradable particulate organic nitrogen concentration in influent (mgN/ℓ)
N_s	=	nitrogen required for sludge production (mgN/ℓ influent)
N'_{ti}	=	nitrogen available for nitrification
	=	$N_{ti}-N_s$ (mgN/ℓ influent)
O	=	general parameter for oxygen
O_c,O_n O_d,O_t		Subscripts c, n, d and t refer respectively to the oxygen demands for carbonaceous material degradation, nitrification, that recovered by denitrification and total
O_i,O_a,O_s		Subscripts a and s refer respectively to the dissolved oxygen concentrations in the influent a- and s-recycles
OUR	=	oxygen utilization rate (mgO/ℓ/hr)
P_f	=	excess P removal propensity factor (mgCOD/ℓ)
P_s	=	phosphorus in daily sludge wastage per ℓ influent flow (mgP/ℓ) i.e. the phosphorus removal from the wastewater
P_t	=	total phosphorus concentration (mgP/ℓ). Additional subscripts i and e refer respectively to influent and effluent
q	=	flow rate for waste sludge from the process reactor (ℓ/d)
Q	=	daily mean influent flow rate (ℓ/d)
r	=	mixed liquor recycle ratio from the anoxic to the anaerobic reactor in the UCT type processes
R_{hn}	=	process total average nominal hydraulic retention time (d)
R_a,R_n	=	general parameters for actual and nominal hydraulic retention times. Subscripts p and s refer to primary and secondary anoxic reactors

R_s = sludge age (d)

R_{sm} = minimum sludge age for nitrification

s = underflow recycle ratio

S_f = factor of safety with respect to nitrification

S_{fd} = factor of safety with respect to conversion of a UCT process to a Modified UCT process

S = general parameter denoting COD concentration

S_b
S_u
S_t

Subscripts b, u and t refer respectively to biodegradable, unbiodegradable and total

Additional subscripts i and e refer respectively to concentrations in the influent and effluent

S_{bs}
S_{up}
S_{bi}
S_{bsi}

S_{bsa} = readily biodegradable COD concentration in the anaerobic reactor

S_{COD} = substrate concentration with respect to COD

S_{BOD} = substrate concentration with respect to BOD

SUR = substrate utilization rate

Subscripts a, v and 5 refer respectively to the rate with respect to active, volatile and total sludge concentrations

Additional subscripts COD and BOD refer to the rate with respect to the substrate measurement in terms of COD or BOD

t = time

t_1 = duration of first phase of denitrification in the primary anoxic reactor

U_o, U_u = overflow and undeflow velocity in the secondary settling tank (m/d)

v = volume of waste sludge abstracted from process reactor per day

V = general parameter denoting volume

Subscripts p and r refer respectively to the process total and reactor

V_s = gravity settling velocity of sludge (m/d).

Additional subscripts denote velocity at specified sludge concentrations

X = general parameter denoting sludge mass concentration

Subscripts a, e, i, v, t and n refer respectively to active, endogenous, inert, volatile, total and nitrifier sludge concentrations

Additional subscripts f and i, and a, d and b refer respectively to concentrations in effluent and influent and those in the anaerobic, anoxic and aerobic reactors

$\bar{X}_t$ = process average total sludge concentration (mgTSS/ℓ)

X = for settling tank theory denotes total MLSS sludge concentration (kgMLSS/m³)

Subscripts af, dz, ef, l, o and r refer respectively to the sludge concentration of the layer above the feed point, the dilute zone below the feed point, the effluent, the limiting zone, in the biological reactor and the underflow sludge return

Y_h = heterotrophic organism yield coefficient = 0,45 mgVSS/mgCOD

Y_n = nitrifier organism yield coefficient = 0,10 mgVSS/mgN

α = denitrification attributable to the readily biodegradable COD ($mgNO_3$-N/mg biodegradable influent COD)

γ = coefficient of excess phosphorus removal (mgP/mgVASS) i.e. the proportion of phosphorus in the active mass

Δ = prefix denoting the change in the parameter following

ϕ_{ns} = pH sensitivity parameter for nitrification in the simplified Arrhenius equation = 2,35

μ_n = specific growth rate of the nitrifiers (/d)

Subscript m denotes the maximum rate

Additional subscripts T and 20 refer respectively to the rate at T°C and 20°C

Additional subscripts pH and 7,2 refer respectively to the rate at different pH values and at pH 7,2

2,86 = oxygen equivalent of nitrate i.e. 2,86 mg oxygen can accept as many electrons as 1 $mgNO_3$-N nitrate

8,6 = mg mass of COD utilized per $mgNO_3$-N nitrate denitrified

4,57 = mg mass of oxygen required for nitrifying 1 mgN ammonia to 1 mgN nitrate

, = decimal place

· = multiplication symbol

APPENDIX 2

BRIEF DESCRIPTION OF THE DETERMINATION OF THE READILY BIODEGRADABLE COD FRACTION OF A MUNICIPAL WASTEWATER

1. INTRODUCTION

In the experimental investigation into the dynamic behaviour of the activated sludge process (Dold, Ekama and Marais, 1980), it was found that in the aerobic completely mixed process at short sludge ages (1,5 to 3 days) under daily cyclic square wave loading conditions (feed 12 hours on, 12 hours off), there is a precipitous decrease in oxygen consumption rate immediately after the termination of the feed period (see Fig A2.1). In modelling the activated sludge process, it was found that this behaviour was due to the readily biodegradable COD in the influent; at feed termination, the addition of readily biodegradable COD stops so that the utilization of the readily biodegradable COD stops causing a step change in the oxygen consumption rate. Hence a method for determining the readily biodegradable COD in the influent is the measurement of the step change in oxygen consumption rate at feed termination in a daily cyclic square wave loaded completely mixed process operated at a very short sludge age.

2. APPARATUS

The test is performed using a single reactor completely mixed aerobic activated sludge unit operated at a sludge age of about 1,5 to 3 days depending on the temperature; the higher the temperature the shorter the sludge age, the data shown in Fig A2.1 are from a 2,5 day sludge age unit at 20°C. A schematic representation of the process is shown in Fig A2.2 below.

The following points warrant notice regarding the setting up and operation of the process:

(1) Aeration. The most convenient method of supplying aeration is to use an ordinary fish tank air pump with a fine bubble sparger stone attached to a perspex tube. By adjusting the depth of

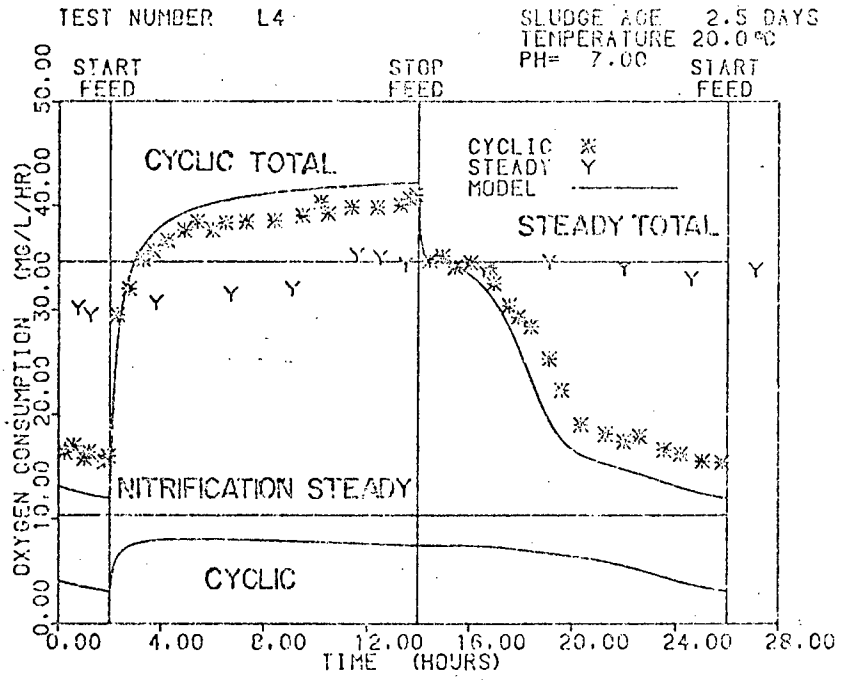

Fig A2.1 *Experimental (and theoretical) oxygen consumption rate over a 26 hour period in a single completely mixed aerobic activated sludge process at 2,5 days sludge age and 20°C under daily cyclic square wave loading conditions (12 hours on, 2 to 14 hours and 12 hours off, 14 to 26 hours). Note precipitous decrease in the measured rate at feed termination (14h00) but that the oxygen consumption rate for nitrification does not change (theoretical line). Experimental (and theoretical) data for the equivalent steady state process (i.e. receiving the same feed volume of 24 hours) are also shown (from Dold, Ekama and Marais 1980).*

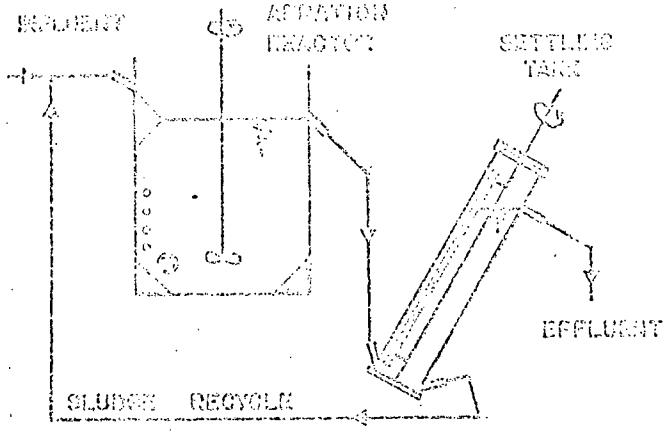

Fig A2.2 *Schematic layout of process configuration.*

immersion of the sparger the D.O. level can be controlled to the desired value of about 2 mgO_2/ℓ.

(2) Inlet and outlet from aeration reactor. All streams to and from the reactor should enter the reactor below the liquid surface and not be dripped into the reactor; dripping feed into the reactor may result in incorrect readings by exposing the feed to air and allowing D.O. entrainment via the liquid/air interface.

(3) Mixing. The contents of the feed tank should be stirred slowly and gently in order to keep particulate matter in suspension, but to avoid excessive D.O. entrainment into the reactor contents. Covering the reactor contents by floating on it a Sagex disc is a very effective method for stopping D.O. Entrainment into the reactor caused by mixing.

(4) Sludge Wastage. In order to maintain the correct sludge age, the correct volume of mixed liquor must be withdrawn daily from the reactor. Say the reactor volume is 10ℓ and the sludge age is to be 2,5 days, then 10/2,5 = 4,0ℓ of mixed liquor needs to be wasted daily. Becuase this volume constitutes a large proportion of the volume of the reactor, (this would be the case up to about 10 days sludge age) the sludge is best wasted with the aid of a pump which is activated by a timer. The wastage arrangement should be such that about 0,3 to 0,5ℓ is abstracted over a few minutes and repeated every few hours. The high rate of abstraction is necessary to avoid settlement of the sludge from the abstraction tube back into the reactor; if this occurs the correct sludge age would not be established. In setting up the sludge wastage system, it is recommended that about 0,5ℓ less than the required volume is withdrawn so that the exact volume can be made up by hand. Also note that if sludge is abstracted when the influent feed is stopped, the reactor volume will be reduced. Consequently it is best not to waste sludge during the non-feed period.

3. METHOD

3.1 Unit Start-up

From start up, operate the unit under constant flow and load

conditions for at least 3 sludge ages allowing the unit to reach steady state - steady state is achieved when the daily oxygen consumption rate and reactor MLVSS concentration show approximately steady values. When steady state is achieved switch the unit over to daily cyclic square wave loading conditions by discharging the daily volume of feed over say 12 hours instead of 24. (Keep the feed volume and COD concentration constant; simply increase the flow rate). Operate the unit under square wave conditions for about 2 sludge ages. Note that now the oxygen consumption rate will vary over the day but the MLVSS concentration should not change significantly.

3.2 Readily Biodegradable COD Measurement

(1) At some time at least 6 hours after commencing the feed, measure the oxygen utilization rate (OUR) by raising the D.O. to about 6 mgO/ℓ, switching off the air supply, and monitoring the rate of decrease of D.O. on a recorder. Measure the OUR every 20 to 30 minutes for about 2 hours before the feed is terminated.

(2) Switch off the *feed* to the reactor and again raise the D.O. to about 6 mgO/ℓ. About 1 to 2 minutes after the feed has been stopped again measure the OUR. Measure the OUR every 20 to 30 minutes for about 2 hours after the feed has been terminated.

(3) Restart the feed and run plant for about 4 hours before repeating the measurement to allow the OUR to stabilize to the feeding condition again.

(4) Plot OUR for each period of about 2 hours before and after the feed was terminated. Estimate the average OUR before and after the feed termination.

4. CALCULATION

The following information is required to calculate the concentration of readily biodegradable COD in the influent feed:

Q = feed flow rate (ℓ/d) over the 3 hour period before the feed is terminated

V_p = reactor volume (ℓ)

OUR_b = average OUR before feed termination (mgO/ℓ/hr)

OUR_a = average OUR after feed termination (mgO/ℓ/hr)

S_{ti} = total influent COD concentration of feed

$\Delta OUR = (OUR_b - OUR_a)$ (mgO/ℓ/hr)

Then the influent readily biodegradable COD concentration

$$S_{bsi} = (\Delta OUR.V_p 24)/(Q.0,334)$$

where

24 = number of hours per day

0,334 = general conversion factor for COD to oxygen. This factor states that for every unit of COD utilized by the micro-organisms, 0,334 units of COD are oxygen consumption and the remaining 0,666 units of COD are converted to new organism mass (see Chapter 1).

The influent readily biodegradable COD fraction with respect to the total COD (f_{ts}) is given by

$$f_{ts} = S_{bsi}/S_{ti}$$

and the influent readily biodegradable COD fraction with respect to the biodegradable COD (f_{bs}) is given by

$$f_{bs} = S_{bsi}/S_{bi}$$

$$= S_{bsi}/S_{ti}(1-f_{us}-f_{up}).$$

3.3 Example calculation

The following data were obtained from an experimental unit operated on primary settling tank effluent at the Goudkoppies plant

Q = 50 ℓ/d for period prior to feed termination

V_p = 7,5ℓ

OUR_b = 24,1 mgO/ℓ/hr

OUR_a = 20,1 mgO/ℓ/hr

S_{ti} = 370 mgCOD/ℓ

$\Delta OUR = 24,1 - 20,1 = 4,0$ mgO/ℓ/hr

$S_{bsi} = (4,0.7,5.24)/(50.0,334)$

$= 47,5$ mgCOD/ℓ

$S_{bs}/S_{ti} = 47,5/370 = 0,13$ mgCOD/mgCOD

$f_{bs} = 47,5/[370(1-0,09-0,04)]$

$= 0,15$ mgCOD/mgCOD.

4. NOTES

(1) Suggested loading: The COD load on the reactor should be such that the OUR (excluding nitrification which may or may not occur at the short sludge age depending on μ_{nm}) is greater than 25 mgO/ℓ/hr. This can be achieved if the feed rate, COD feed concentration and reactor volume are such that the load is greater than 2400 mgCOD/ℓ reactor/day. Thus, if the feed concentration is about 350 mgCOD/ℓ and a reactor volume of 10ℓ is used the feed flow rate Q prior to feed termination should be greater than 2400.10/350 = 68,5ℓ/d.

(2) Nitrification: The degree of nitrification which takes place in the unit does not affect the readily biodegradable COD determination (see Fig A2.1). This is because at the short sludge ages at which the determination is done, the oxygen utilization for nitrification is the same before and after feed termination due to the high ammonia concentration in the reactor and effluent. If the ammonia concentration in the reactor and effluent before and after feed termination is low (< 5 mgN/ℓ), the change in the oxygen utilization rate for nitrification may lead to errors in the readily biodegradable COD determination.

5. SUGGESTED READING

1. An understanding of the paper "A General Model for the Activated Sludge Process" by Dold, Ekama and Marais (1980) (Prog.Wat.Tech., 12, 47-77) is strongly recommended as background information.

2. Further detail on the operation of the experimental units

is given by Marais and Ekama (1976) "The Activated Sludge Process Part I - Steady State Behaviour". Water S A, 2, 4, 163-200.

3. A detailed discussion on the method and possible errors that can be incurred in measuring the oxygen consumption rate is given by Ekama and Marais "Letter to the Editor", Water S A, 5, 1, 57-60.

APPENDIX 3

BRIEF DESCRIPTION OF THE DETERMINATION OF THE MAXIMUM SPECIFIC GROWTH RATE OF THE NITRIFIERS (μ_{nm})

1. INTRODUCTION

The maximum specific growth rate constant of the nitrifiers (μ_{nm}) defines the maximum rate at which the nitrifying organisms can grow in the activated sludge process. Although μ_{nm} is a kinetic "constant" in the nitrification theory, its magnitude can differ appreciably between different municipal wastewaters, and can vary even between batches of the same wastewater. This behaviour is so marked that μ_{nm} should be classified as a wastewater characteristic.

The magnitudes of μ_{nm} that have been observed in municipal wastewaters at 20°C range from 0,30 to 0,65 per day. The low values appear to be due to inhibition by some substance(s) in the wastewater. These substances are more likely to be present in wastewaters having significant industrial* contributions; in general, the greater the contribution, the lower the μ_{nm} value. The reduction in μ_{nm} is not the result of toxicity because a high efficiency of nitrification can be achieved provided the sludge age is sufficiently long - toxicity would tend to terminate nitrification irrespective of sludge age.

The magnitude of μ_{nm} has a significant effect on the minimum sludge age for nitrification R_{sm}; the lower μ_{nm}, the longer R_{sm}. Clearly, due to the link between the wasteflow composition and μ_{nm}, an experimental estimate of the μ_{nm} value is important for efficient design of nitrifying plants. A method for estimating μ_{nm} is set out below.

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*The type of industry referred to here are those which produce effluents which have high metal ion concentrations e.g. metal finishing industry, plating works, paint production, tannery wastes, etc.

2. METHOD AND APPARATUS

2.1 General

The test is performed in a single completely mixed reactor at about 6 to 10 days sludge age receiving a constant flow and load but with alternating cycles of anoxic and aerobic periods of 2 to 3 hours each. The selection of the sludge age depends on two factors, (i) the temperature of the wastewater and (ii) whether or not the μ_{nm} value is expected to be high (0,5/d at 20°C) or low (0,2/d at 20°C). The higher the temperature the shorter the sludge age, and the lower the expected μ_{nm} value the longer the sludge age.

The minimum sludge age for nitrification R_{sm} at T°C is given by (see Chapter 5, Section 4.4)

$$R_{sm} = S_f / \{\mu_{nmT} (1-f_t) - b_{nT}\} \qquad (A3.1)$$

where

μ_{nmT} = maximum specific growth rate at T°C

$$= \mu_{nm20}(1,123)^{(T-20)} \qquad (A3.2)$$

μ_{nm20} = rate at 20°C

b_{nT} = endogenous respiration rate of the nitrifiers at T°C

$$= 0,04(1,029)^{(T-20)} \qquad (A3.3)$$

T = temperature in deg C.

S_f = factor of safety to ensure complete nitrification, usually 1,25.

f_t = fraction of the total time that the process is under anoxic conditions.

With the aid of Eqs (A3.1 to A3.3), the sludge age required for nitrification in the process can be estimated for an expected μ_{nm20} value, and generally for μ_{nm20} around 0,40/d will be found to be between 6 to 10 days at 20°C for a 2 hourly cycle of anoxic and aerobic periods (f_t = 0,50).

The length of the anoxic and aerobic cycles is chosen such that the concentration of ammonia during the aerobic period *does not decrease below 2 mgN/ℓ.* The reason for this is that if the ammonia concentration is greater than 2 mgN/ℓ, the nitrification rate proceeds at the maximum possible and the production rate of nitrate can be directly linked to μ_{nm}; if the ammonia concentration is below 2 mgN/ℓ, the nitrate production rate no longer can be directly linked to μ_{nm} because now the limited supply of ammonia reduces the nitrification rate even though the μ_{nm} value remains unchanged (see Fig 5.1 in Chapter 5). If it is found that the ammonia concentration reduces to below 2 mgN/ℓ in too short a time interval, the sludge age should be reduced. This has the effect of reducing the concentration of nitrifying organisms, with the result that less ammonia can be nitrified per unit time.

The experimental data shown in Fig A3.1 were measured at 6 days sludge age and 20°C with an anoxic and aerobic cycle of 2 hours each. The data are tabulated in Table A3.1

A schematic representation of the experimental process and some points regarding its operation are given in Appendix 2.

2.2 Experimental Unit Start-Up

From start-up, operate the unit under constant flow and load conditions at the selected sludge age under *purely aerobic conditions* for about 2 to 3 sludge ages by which time nitrification should be taking place.* If necessary operate for 1 or 2 sludge ages longer to ensure nitrification is complete and the nitrifiers are well established in the process. Only when nitrification is

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*A simple qualitative test to check the presence of nitrate is the Merckoquant® paper test, or to leave a 100 mℓ (or larger) measuring cylinder with mixed liquor standing overnight; if upon tapping the cylinder, bubbles are released from the sludge layer, or some sludge has risen to the surface, nitrification is taking place - evidenced by the nitrogen bubbles released by denitrification of the nitrate in the sludge layer.

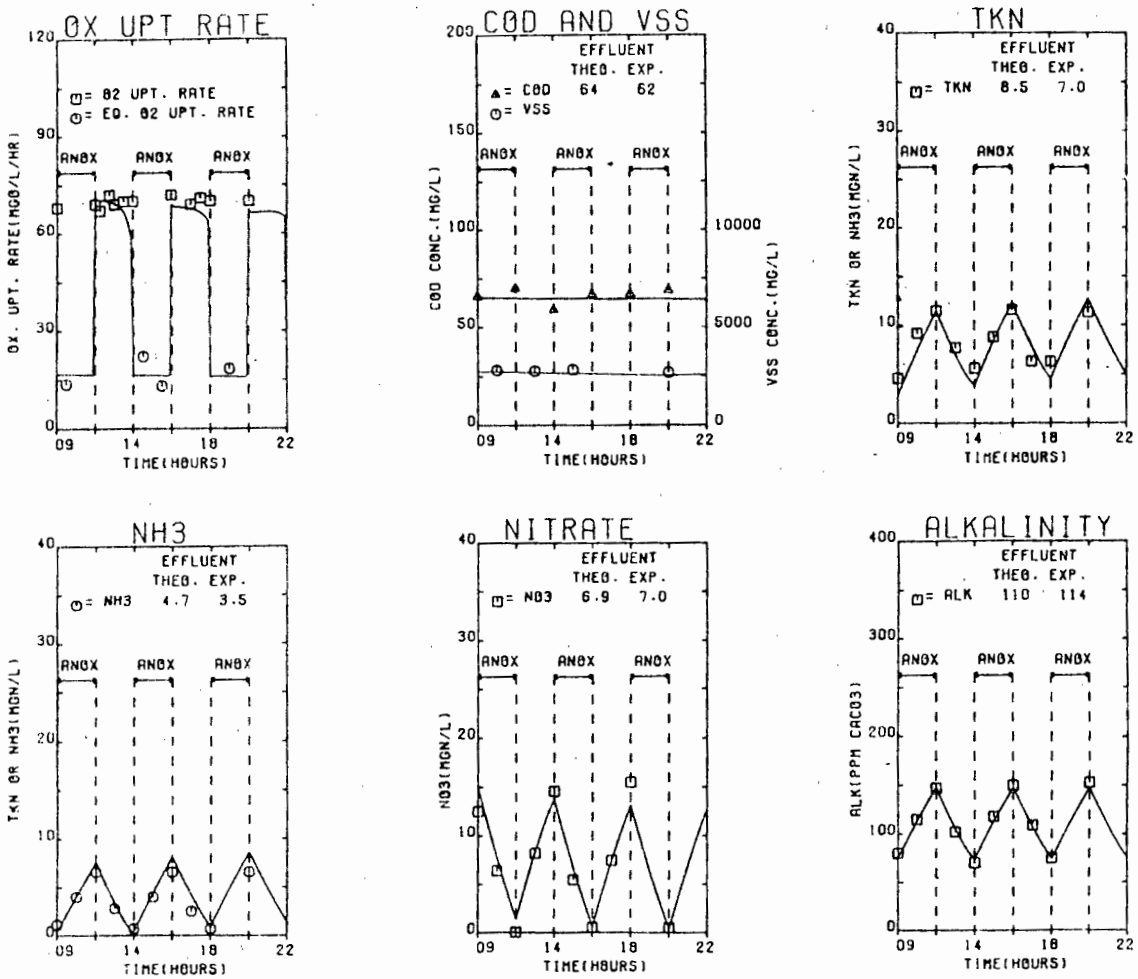

Fig A3.1 *Experimental (and theoretical) data of (a) the oxygen consumption rate, (b) reactor MLVSS concentration and filtered COD concentration and filtered reactor, (c) TKN, (d) ammonia, (e) nitrate and (f) Alkalinity concentrations versus time in a 2 hourly alternating anoxic and aerobic process under constant flow and load conditions at 20°C and 6 days sludge age. (from van Haandel and Marais 1981).*

Table A3.1 Experimental data measured in a 2 hourly alternating anoxic-aerobic process at 6 days sludge age and 20°C.

Process Parameters

Reactor Volume = 6ℓ
Influent flow = 20ℓ/d
Sludge age = 6 days
Temperature = 20°C
Recycle ratio = 1:1

Day's average			COD	TKN	NH_3	Alk	NO_3	pH
Influent (unfilt.)			492	49,0	33,5	245	-	7,8
Effluent (unfilt.)			62	7,1	3,5	114	7,1	7,5
Effluent (filt.)			54	6,9	3,5	114	5,8	-
TIME	OCR	VSS	COD	TKN	NH_3	Alk	NO_3	pH
9h30†	68	-	66	4,6	1,1	80	12,5	7,1
10h30	-	2822	-	9,2	4,0	115	6,4	7,2
11h30*	69	-	70	11,5	6,6	147	0,0	7,4
11h45	67	-	-	-	-	-	-	-
12h15	72	-	-	-	-	-	-	-
12h30	69	2773	-	7,7	2,8	102	8,2	7,2
13h00	70	-	-	-	-	-	-	-
13h30†	70	-	59	5,6	0,7	70	14,6	7,1
14h30	-	2832	-	8,8	4,0	118	5,5	7,2
15h30*	72	-	67	8,6	6,6	150	0,5	7,4
16h30	69	-	-	6,3	2,5	109	7,5	-
17h00	71	-	-	-	-	-	-	-
17h30†	70	-	67	6,3	0,7	75	15,5	-
19h30*	70	2692	69	11,3	6,6	153	0,5	-

* start of aerobic period

† start of anoxic period

complete should the process be switched over to the alternating aerobic-anoxic phase, say two hours aerobic, two hours anoxic. Even for very low values of μ_{nm} (0,20 at 20°C), it is unlikely that nitrification will not take place at sludge ages around 10 days at 20°C with 50% anoxic times. Operate the process under alternating conditions for not less than one sludge age to allow the system to stabilize to the alternating conditions.

During the stabilization period, measure on a daily basis the following -

i) influent COD and TKN concentration

ii) reactor MLVSS concentration and pH

iii) effluent* TKN, ammonia, nitrate concentrations

iv) effluent* COD concentration.

* Grab samples collected from the effluent bucket after a full 24 hour period.

When these data show approximate stability over a period of about one sludge age, the system can be considered to be stable and the analyses for the μ_{nm} determination can be commenced.

2.3 Analysis requirement for μ_{nm} measurement

Once the process is operating satisfactorily, an intensive testing programme of about 14 to 16 hours is performed on it. The data measured during such programme are the following:

a) grab samples from influent and effluent buckets over 24 hour period during which testing period occurs;

i) unfiltered influent: COD, TKN, NH_3, Alk and pH

ii) unfiltered effluent: COD, TKN, NH_3, Alk and pH

iii) filtered effluent: COD, TKN, NH_3, Alk, NO_3 and pH.

b) on grab samples from the reactor:

i) samples at hourly intervals, filtered TKN, NH_3, NO_3, Alk and pH

ii) samples at 2 to 3 hourly intervals, MLVSS and filtered COD.

c) on reactor every ½ hour during aerobic periods:

i) oxygen consumption rate.

As an example of the data measured during an intensive testing programme, the data plotted in Fig A3.1 are listed in Table A3.1.

3. THEORY AND CALCULATION

The μ_{nm} value is calculated from the increase in the nitrate concentration during the aerobic stages of the alternating cycle. From increase in the nitrate concentration the nitrification rate of the nitrifying organisms r_{Nn} can be calculated, and provided the ammonia concentration does not decrease below about 2 mgN/ℓ, this rate is directly linked to μ_{nm} i.e.

$$\mu_{nm} = r_{Nn}\ Y_n/X_n \quad (/d) \qquad (A3.4)$$

where

r_{Nn} = nitrification rate by the nitrifying organisms in mg NO_3-N/ℓ reactor volume/day

Y_n = yield coefficient for the nitrifiers

= 0,10 mgVSS/mgNO_3-N nitrified

X_n = reactor nitrifier VSS concentration (mgVSS/ℓ).

The nitrifier sludge concentration is calculated from the nitrate concentration generated per litre influent. Note that this concentration is not equal to the nitrate concentration in the effluent because during the anoxic periods nitrate is removed from the system by denitrification. An estimate of the nitrate generated per litre influent, N_{ng}, is found from the following equation:

$$N_{ng} = N_{ti} - N_{te} - N_s \quad (mgN/\ell) \qquad (A3.5)$$

where

N_{ng} = nitrate generated per litre influent (mgN/ℓ)

N_{ti} = influent TKN concentration (mgN/ℓ)

N_{te} = effluent TKN concentration (mgN/ℓ)

N_s = nitrogen required for sludge production (mgN/ℓ influent)

$$= f_n \frac{V_p X_v}{Q.R_s} \quad (mgN/\ell) \qquad (A3.6)$$

f_n = nitrogen content of the VSS

= 0,10 mgN/mgVSS

V_p = volume of the reactor (ℓ)

X_v = average VSS concentration over testing period (mgVSS/ℓ)

Q = influent flow rate (ℓ/d)

R_s = sludge age (d).

Knowing N_{ng}, the concentration of nitrifier sludge mass in the reactor is given by

$$X_n = \frac{Y_n (N_{ng}) R_s}{(1 + b_{nT}R_s)R_{hn}} \quad (mgVSS/\ell) \qquad (A3.7)$$

where

R_{hn} = nominal retention of the process

$= V_p/Q$ (d).

The increase in the nitrate concentration in the reactor during aerobic period r_{Nr} is the net effect of two reactions (i) the increase in nitrate by nitrifying organisms which is the r_{Nn} rate required for the μ_{nm} determination and (ii) the change in nitrate

concentration in the reactor caused by nitrate leaving the system via the effluent, i.e. hydraulic effects, r_{Nh}, i.e.

$$r_{Nn} = r_{Nr} + r_{Nh} \qquad \text{(A3.8)}$$

Taking a time interval of $\Delta t = t_2 - t_1$ during the aerobic period where t_1 and t_2 are the beginning and end respectively of the time interval, and the nitrate concentrations in the reactor at times t_1 and t_2 are N_{n1} and N_{n2} mgN/ℓ respectively, then the net rate of nitrate increase per litre reactor volume

$$r_{Nr} = (N_{n2} - N_{n1})/(t_2 - t_1) \cdot (\text{mgN}/\ell/\text{d}) \qquad \text{(A3.9)}$$

The rate at which nitrate leaves the reactor per litre reactor volume at a time instant is simply the product of effluent flow and the concentration of nitrate at the time instant divided by the reactor volume i.e. at time t_1 $r_{Nh1} = Q.N_{n1}/V_p = N_{n1}/R_{hn}$. Similarly at t_2 $r_{Nh2} = N_{n2}/R_{hn}$. Now the rate of nitrate leaving the reactor *during* the time interval bounded by t_1 and t_2 can be approximated by the average rates at times t_1 and t_2. Hence the average nitrate loss over the interval Δt due to hydraulic effects is given by

$$r_{Nh} = (N_{n1} + N_{n2})/(2\ R_{hn}) \quad (\text{mgN}/\ell/\text{d}) \qquad \text{(A3.10)}$$

The hydraulic effect causes the rate of nitrate generation to decrease so that this rate must be added to the rate of nitrate generation measured from the nitrate concentrations in the reactor as given by Eq (A3.8).

It should be noted that although only the nitrate concentrations during the aerobic cycles are used for the determination of μ_{nm}, the other analyses are useful to check that the experiment has progressed satisfactorily. These data can be used to determine and/or check constants other than μ_{nm}; the nitrate concentrations during the anoxic cycles can be used to determine the 2nd rate of denitrification in the primary anoxic reactor (K_2), but this determination

requires a knowledge of the readily biodegradable COD concentration of the influent (f_{bs}). Also the Alkalinity values during the aerobic and anoxic periods can be used to check the μ_{nm} and K_2 determinations. For details see van Haandel and Marais (1981).

When all the data is measured, the constants can be determined and/or checked with the aid of computer simulation (see Fig A3.1). However, computer simulation is not essential because generally it has been found that when the manually calculated values of μ_{nm} (and K_2) are used in the simulation, very good correspondence with the experimental data is obtained.

4. EXAMPLE

To demonstrate the calculations, the μ_{nm} value will be calculated from the data listed in Table A3.1.

The nitrate concentrations measured at hourly intervals during the aerobic periods are listed in Table A3.2. From these data, the reactor nitrate generation rate r_{Nr} and the rate of nitrate loss by hydraulic effects r_{Nh} are calculated from Eqs (A3.9 and A3.10) respectively. The sum of the two rates gives the rate of nitrate generation by the nitrifiers r_{Nn} i.e. Eq (A3.8). From the 4 periods of one hour, a mean value of r_{Nn} is 8,45 mgNO_3-N/litre reactor volume/hour is found.

The average MLVSS concentration during the experiment is 2780 mgVSS/ℓ. From this, the nitrogen required for sludge production N_s is determined from Eq (A3.6) i.e.

$$N_s = 0{,}10\,\frac{6.2780}{20.6} = 13{,}9 \text{ mgN/ℓ influent flow.}$$

The average effluent TKN concentration (unfiltered) is 7,1 mgN/ℓ. Hence from Eq (A3.5), the nitrate generated per litre influent, N_{ng}, is

$$N_{ng} = 49{,}0 - 7{,}1 - 13{,}9 = 28{,}0 \text{ mgN/ℓ.}$$

At 6 days sludge age and measured temperature 20°C, the

Table A3.2 Calculation of nitrification rates from nitrate concentration profiles during the aerobic period of an alternating anoxic-aerobic completely mixed process under constant flow and load.

Time	NO_3	r_{Nr}^{*}	$r_{Nh}^{*\dagger}$	r_{Nn}^{*}
11h30	0,0			
		†8,2	†0,57	†8,77
12h30	8,2			
		†6,4	†1,58	†7,98
13h30	14,6			
15h30	0,5			
		†7,0	†0,56	†7,56
16h30	7,5			
		†8,0	†1,60	†9,60
17h30	15,5			
Mean				†8,45

* units $mgNO_3$-N/ℓ reactor volume/h.

† nominal hydraulic retention time = 6/20 = 0,30d ≡ 7,2h.

nitrifier concentration in the reactor is found from Eq (A3.7)

$$X_n = \frac{0,10.28.6}{(1 + 0,04.6)\ 6/20} = 45,2 \text{ mgVSS}/\ell$$

Hence from Eq (A3.4), the maximum specific growth rate of the nitrifiers μ_{nm} at 20°C is

$$\mu_{nm} = (8,45.24).0,10/45,2$$

$$= 0,45 \text{ /d. at } 20°C$$

Hence $\mu_{nm20} = 0,45/d.$

If in this example, the temperature was not 20°C, the endogenous respiration rate in Eq (A3.7) for X_n needs to be adjusted with Eq (A3.3) for the given temperature. The value of μ_{nm} found from Eq (A3.4) is rate at the given temperature and to calculate μ_{nm20}, this value needs to be adjusted to 20°C with Eq (A3.2).

5. REFERENCES

1. van Haandel A C and G v R Marais (1981) "Nitrification and denitrification kinetics in the activated sludge process", Research Report W 39, Dept. of Civil Eng., Univ. of Cape Town.

2. Sehayek E and G v R Marais (1981) "Kinetics of biological nitrogen removal in the activated sludge process", Research Report W 41, Dept. of Civil Eng., Univ. of Cape Town.

3. Further detail on the operation of laboratory units is given by Marais and Ekama (1976) "The activated sludge process Part I - steady state behaviour", Water SA, 2, 4, 163-200.